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Review of the Environmental Fate of Selected Chemicals

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ABSTRACT

A review of the recent literature on sources, production, environmental fate, and bioaccumulation has been carried out by SRI on 26 classes of compounds. These included epoxides, haloolefins, aldehydes, alkyl and benzyl halides, peroxides, hydroperoxides and peracids, polyhalomethanes, aromatic amines, polychlorinated biphenyls, azo dyes, carbamic acid esters, hydrazines, acyl halides and ketene, phosphoric acid esters, aziridines, lactones, alkyl sulfates, sultones, aryl dialkyltriazenes, diazoalkanes, haloalcohols, haloethers, hydroxylamines, nitrosamines, nitrofurans, and azides.

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A review of the recent literature on sources, production, environmental fate, and bioaccumulation has been carried out by SRI on 26 classes of compounds. These included epoxides, haloolefins, aldehydes, alkyl and benzyl halides, peroxides, hydroperoxides and peracids, polyhalomethanes, aromatic amines, polychlorinated biphenyls, azo dyes, carbamic acid esters, hydrazines, acyl halides and ketene, phosphoric acid esters, aziridines, lactones, alkyl sulfates, sultones, aryl dialkyltriazenes, diazoalkanes, haloalcohols, haloethers, hydroxylamines, nitrosamines, nitrofurans, and azides.

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1. INTRODUCTION

The Office of Toxic Substances (OTS), U.S. Environmental Protection Agency (EPA), requested SRI to conduct a literature search and evaluation of the results for the suspected carcinogens listed in Table 1. The EPA is concerned with information and estimates of the entry and behavior of these compounds in the environment. A literature search was conducted to determine what information is available on these compounds to attempt to predict their environmental fates and the likelihood of their accumulation in mammals, particularly humans.

The fate of chemicals in the environment depends on a variety of chemical, physical, and biological interactions, few of which have been studied in enough detail to predict either the dominant pathways for transformation or the rates of change in concentration associated with those pathways. Previous studies have shown that it is difficult to determine losses of material from manufacturing sites and that the eventual fate of the material in the environment cannot be predicted on the basis of published information. However, some intelligent guesses can be made based on structural analogies within classes of compounds. For this purpose, emphasis was placed on searching for or estimating kinetic values for potentially important pathways of chemical degradation, including free radical oxidation, photolysis, and hydrolytic reactions. Partition coefficients (octanol/water) were calculated for each compound as one measure of the propensity for biological uptake. Literature reports on biological uptake and metabolism of these compounds were also reviewed and evaluated.

Table 1

SUSPECTED CARCINOGENS STUDIED

Class/Name	CAS Number	Formula
Epoxides		
Ethylene oxide	75-21-8	C_2H_4O
Propylene oxide	75-56-9	C_3H_6O
Epichlorohydrin	106-89-8	C_3H_5ClO
Styrene oxide	96-09-3	C_8H_8O
Glycidol	556-52-5	$C_3H_6O_2$
Glycidaldehyde	765-34-4	$C_3H_4O_2$
Haloolefins		
Vinyl chloride	75-01-4	C_2H_3Cl
Trichloroethylene	79-01-6	$C_2H_3Cl_3$
Vinylidene chloride	75-35-4	$C_2H_2Cl_2$
Chloroprene	126-99-8	C_4H_5Cl
Aldehydes		
Formaldehyde	50-00-0	CH_2O
Acrolein	107-02-8	C_3H_4O
Dihaloalkanes		
1,2-Ethylene dibromide	106-93-4	$C_2H_4Br_2$
1,2-Ethylene dichloride	107-06-0	$C_2H_4Cl_2$
Polyhalomethanes		
Carbon tetrachloride	56-23-3	CCl_4
Chloroform	67-66-3	$CHCl_3$

Table 1 (continued)

SUSPECTED CARCINOGENS STUDIED

Class/Name	CAS Number	Formula
Peroxides		
Cumene hydroperoxide	80-95-9	$C_9H_{12}O_2$
Di-tert-butyl peroxide	110-05-4	$C_8H_{18}O_2$
Hydrogen peroxide	7722-84-1	H_2O_2
tert-Butyl hydroperoxide	75-9-2	$C_4H_{18}O_2$
Succinic acid peroxide	3504-13-0	$C_4H_6O_5$
Alkyl halides and benzyl halides		
Benzyl chloride	100-44-7	C_7H_7Cl
Methyl chloride	74-87-3	CH_3Cl
Aromatic amines		
4,4'-Methylenebis(2-chloroaniline)	101-14-4	$C_{13}H_{12}Cl_2N_2$
1-Naphthylamine	134-32-7	$C_{10}H_9N$
3,3-Dichlorobenzidine	91-94-1	$C_{12}H_{10}Cl_2N_2$
Benzidine	92-87-5	$C_{12}H_{12}N_2$
2-Biphenylamine	90-41-5	$C_{12}H_{11}N$
4-Biphenylamine	92-67-1	$C_{12}H_{11}N$
4,4'-Methylenebis(2-methylaniline)	838-88-0	$C_{15}H_{18}N_2$
2-Naphthylamine	91-59-8	$C_{10}H_9N$
Polychlorinated biphenyls		
Tetrachlorobiphenyl[a]	26914-33-0	$C_{12}H_6Cl_4$
Pentachlorobiphenyl[a]	25429-29-2	$C_{12}H_5Cl_5$
Hexachlorobiphenyl[a]	59291-64-4	$C_{12}H_4Cl_6$

Table 1 (continued)

SUSPECTED CARCINOGENS STUDIED

Class/Name	CAS Number	Formula
Azo dyes		
Azobenzene	103-33-3	$C_{12}H_{10}N_2$
4-Aminoazobenzene	60-09-3	$C_{12}H_{11}N_3$
4-Dimethylaminoazobenzene	60-11-7	$C_{14}H_{15}N_3$
2-Methyl-4-[(2-methylphenyl)azo]-benzenamide	97-56-3	$C_{14}H_{15}N_3$
Carbamates		
Ethyl carbamate	51-79-6	$C_3H_7NO_2$
Hydrazines		
Hydrazine	302-01-2	H_4N_2
1,1-Dimethylhydrazine	57-14-7	$C_2H_8N_2$
Hydrazine carboxamide	57-56-7	CH_5N_3O
1,2-Dimethylhydrazine	540-73-9	$C_2H_8N_2$
Acyl chlorides and ketene		
Benzoyl chloride	98-88-4	C_7H_5ClO
Diethylcarbamoyl	88-10-8	$C_5H_{10}ClNO$
Dimethylcarbamoyl chloride	79-44-7	C_3H_6ClNO
Ketene	463-51-4	C_2H_2O
Phosphates		
Triethyl phosphate	78-40-0	$C_6H_{15}O_4P$
Trimethyl phosphate	512-56-1	$C_3H_9O_4P$

Table 1 (continued)

SUSPECTED CARCINOGENS STUDIED

Class/Name	CAS Number	Formula
Aziridines		
Ethylenimine	151-56-4	C_2H_5N
1-Aziridineethanol	1072-52-2	C_4H_9NO
Propylenimine	75-55-8	C_3H_7N
Lactones		
β-Propiolactone	57-57-8	$C_3H_4O_2$
Sulfates		
Dimethyl sulfate	77-78-1	$C_2H_6O_4S$
Diethyl sulfate	64-67-5	$C_4H_{10}O_4S$
Sultones		
1,3-Propane sultone	1120-71-4	$C_3H_6O_3S$
1,4-Butane sultone	1633-83-6	$C_4H_8O_3S$
Aryl dimethyltriazenes		
3,3-Dimethyl-1-phenyltriazene	7227-91-0	$C_8H_{11}N_3$
1-(p-Chlorophenyl)-3,3-dimethyltriazene	7203-90-9	$C_8H_{10}ClN_3$
Diazoalkanes		
Diazomethane	334-88-3	CH_2N_2
Chloroalcohols and Ethers		
2-Chloroethanol	107-09-3	C_2H_5ClO
1-Chloropropanol	127-00-4	C_3H_4ClO
Chloromethylmethyl ether	107-30-2	C_2H_5ClO

Table 1 (concluded)

SUSPECTED CARCINOGENS STUDIED

Class/Name	CAS Number	Formula
Bis(2-chloroethyl)ether	11-44-4	$C_4H_2Cl_2O$
Bis(chloroethyl)ether	542-88-1	$C_2H_4Cl_2O$
Hydroxylamine		
Hydroxylamine	7803-49-8	H_3NO
N-Methylhydroxylamine	593-77-1	CH_5NO
O-methylhydroxylamine	67-62-0	CH_5NO
Nitrosoamines		
N-Nitrosodimethylamine	62-75-9	$C_2H_6N_2$
N-Nitrosodiethylamine	55-18-5	$C_4H_{10}N_2O$
Furans		
2-Nitrofuran	609-39-2	$C_4H_3NO_3$
N-[4-(5-nitro-2-furanyl)-2-thiazolyl]-acetamide	531-82-8	$C_9H_7N_3O_4S$
N-[4-(5-nitro-2-furanyl)-2-thiazolyl]-formamide	24554-26-5	$C_8H_5N_3O_4S$
Azides		
Sodium azide	26628-22-8	N_3Na

---

[a] Only the CAS number for the general compound is given here. Each of these, of course, have numerous isomers with individual CAS numbers.

The sections of the report covering the individual classes of compounds have been ordered according to the production estimates for the class as a whole. Thus, although there are members of the epoxide class having low production estimates, as a whole the production estimate for the entire class places it at the top of the list. Where possible, total production estimates are given for each compound on the list; producers and plant sites are also listed where available. Physical and chemical properties have been included. As requested by OTS, EPA, we have limited discussion to the environmental transformation and bioaccumulation of the compounds and classes of compounds.

2. SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The results of a literature search were combined with estimation procedures to develop reliable information on the manufacture, environmental transformations, and bioaccumulation of over 70 organic compounds. These organic compounds represent 22 classes of chemical structures that are believed to have mutagenic and/or carcinogenic properties.

The objective was to provide the Environmental Protection Agency with information that can be used to better evaluate the probable hazard to human and animal populations from exposure to these specific compounds and to other members of these classes. The rationale for developing this information lies in the belief that hazard ranking must take into account at least three factors: (1) exposure of significant populations of humans or animals to the chemical, as reflected by manufacturing data on total production and location of production facilities; (2) transport, transformation, and persistence, which will govern the levels of exposure in water, soil, or air and will indicate possible geographical distribution from point sources; and (3) bioaccumulation in mammalian species, which together with toxicity or carcinogenicity data can indicate the probable hazard to life.

This study has several limitations: it does not address the questions of toxicity, biodegradation, or the possible hazard of transformation products. Nonetheless, the study does provide a first cut screening of these compounds and some of their homologs to eliminate compounds that clearly do not pose a problem of environmental exposure and to focus attention on those possibly few compounds that are of particular concern on the basis of wide exposure, long persistence, and significant bioaccumulation. This review also draws attention to important gaps in our

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knowledge of these compounds and their interaction with the environment. The following evaluation of relative environmental exposure of the compounds examined in this study is necessarily incomplete and is subject to revision when additional data are developed.

We have prioritized these compounds for overall environmental exposure on the basis that the exposure of human populations to a specific carcinogenic compound is minimal when the compound is manufactured in amounts of less than 10^6 lbs yr^{-1}, used as an intermediate for in-plant conversion, is rapidly transformed in the environment, and does not bioaccumulate. Moderate or severe exposure problems arise from compounds manufactured in large amounts ($> 10^6$ lbs yr^{-1}), the chemicals are end products, are transformed slowly in the environment and bioaccumulate.

Given these limitations, we have classified the compounds into three categories: minimal, moderate, and severe environmental hazards, as summarized below.

(1) Minimal exposure: production of 10^3 to 10^6 lbs yr^{-1} and/or intermediate use only, rapid transformation, and low bioaccumulation. The following compounds were judged to present a minimal hazard:

Diazomethane
Ketene
Bis(chloromethylether)
Chloromethyl methyl ether
Chloroalkyl ethers
Peroxides, including hydrogen peroxide
Other diazoalkanes

(2) Moderate exposure production of 1-4 x 10^6 to 4 x 10^6 lbs yr^{-1}, rapid transformation in the environment, low propensity to bioaccumulate. Compounds judged to present a moderate hazard are:

Chloroform
Formaldehyde
Benzoyl chloride
Most alkyl halides
Lactones
Sulfates
Epoxides
Aziridines
Nitrosamines
Aryl triazenes
Sultones
Hydrazines
Hydroxylamines
Haloolefins

(3) Severe exposure: in excess of 4×10^6 lbs yr^{-1}, slow transformation in the environment, moderate to high propensity to bioaccumulate. Compounds judged to present severe exposure are:

Aromatic amines	Polychlorinated biphenyls
Chloroalcohols	Ethyl aliphatic carbamate
1,2-dihaloalkanes	Azo dyes
Carbon tetrachloride	Phosphate esters

Although they are likely to pose a minimal problem, there were too few data on azide ion or nitrofurans to make even a tentative judgment.

Several of the compounds classified as severe exposure problems, including carbamates, phosphates, amines, and chloroalcohols, may biodegrade at significant rates in soil and water. No information on this subject was sought and is needed to provide more reliable estimates. Several of these same compounds as well as nitrofurans may also be phototransformed at significant rates; data on the uv spectra and quantum yields for these processes are needed.

Estimated half-lives of these compounds in the atmosphere are based on a few good data for rates of reaction of HO radical with olefins, aromatics, and alkanes in the atmosphere, a few data for reactions in solution with more complex compounds, and a number of intelligent guesses about solvent and substituent effects on rates of reaction of HO· with the compounds in this study. The paucity of reliable rate constants for reactions of HO radical with simple functionalized organic compounds in the atmosphere remains a serious gap in our knowledge of the environmental transformation of organic compounds.

In this study we have used the partition coefficients (log P as an index of the propensity of a compound to bioaccumulate on the grounds that, to a first approximation, log P measures the ease of transfer from water to tissue (lipophilicity). However, high lipophilicity may be accompanied by a high rate of metabolism. Thus both factors must be evaluated to determine the actual extent of bioaccumulation for a specific compound. Information of this kind was found for only a few of the compounds examined in this study. Therefore, we recommend that, for compounds that appear to be significant environmental hazards and for which this information is lacking, laboratory animal studies be made of their uptake, distribution, retention, and excretion.

3. METHODOLOGY

Literature Search

The basis for the literature search was the list of suspect carcinogens (Table 1) as supplied by EPA. Chemical Abstracts was searched from 1965 through 1976 for biological and chemical activity of all compounds or classes of compounds. The U.S. Government Reports were searched from 1970 through 1976. Primary sources such as current issues of pertinent journals were scanned. Most of the searching was carried out manually, but Chemical Abstracts, Volume 84, was searched by Chemical Abstract Service (CAS) number using the Systems Development Corporation (SDC) computerized files of Chemical Abstracts.

Manual searching was performed not only under common names and full chemical names, but also under such terms as environmental fate, biodegradation, photolysis, and partition coefficients. The number of references called in the first search varied considerably for each compound or class of compounds. Abstracts were studied to limit the number of full text copies to the most pertinent references only. For some compounds, Chemical Abstracts was searched as far back as necessary to find reliable data for specific chemical processes such as hydrolysis.

Estimation Procedures for Persistence

Kinetic Relationships

Estimates of persistence are conveniently expressed as the half-life ($t_{\frac{1}{2}}$) for a substrate (S) under a specific set of conditions, usually involving one kind of reaction. For the reaction

$$X + S \rightarrow \text{Products}$$

the rate law is

$$dS/dt = k_x[S][X] \qquad (1)$$

Under conditions where X is replaced as consumed, resulting in a constant or steady-state concentration, the second-order relation (1) becomes pseudo-first order and may be readily integrated to give

$$\ln(S_o/S_t) = k_x[X]t + C \qquad (2)$$

where S_o is the initial concentration of S and S_t is the concentration at time t. At one half-life of S, $S_o/S_t = 2$ and

$$t_{\frac{1}{2}} = \ln 2/k_x[X] \qquad (3)$$

If more than one reaction is important for conversion of S, the rate expression and equation (3) are replaced by more general relations in which $k_x[X]$ becomes $K_A[A] + \ldots k_N[N]$, the sum of all pseudo-first-order rates.

Thus, the half-life in the environment for a specific compound (S) can be estimated if the concentration of the reactive species (X) and the rate constant for reaction of X with S are known.

Chemical Transformations in the Environment

At least three important types of transformations of organic compounds in the atmosphere and in aquatic systems can be identified: oxidation by HO, O_3, or RO radicals, hydrolysis, and photolysis.

Oxidation Processes in the Environment

The major oxidizing species in the atmosphere are HO radical and ozone; other intermediate radicals are formed but do not control the rates of oxidation of the initial compound. Our knowledge of the chemistry of aquatic systems is much more uncertain, but estimates of reactivity and concentrations of peroxy and alkoxy radicals ($RO_2\cdot$ and RO•) (where R is H or an organic group) indicate that only RO• (or triplet ketone biradicals) are likely to be important oxidizers in aquatic systems. The concentrations of HO• and O_3 in the atmosphere are probably known accurately within a factor of 3, while the concentrations of RO• in water are only order-of-magnitude estimates.

To calculate persistence in the atmosphere, we have used a concentration of $[HO\cdot] = 0.8 \times 10^{-14}$ M (average for day and night), based on measurements of Wang et al. (1975), which are 5.7 times larger than the earlier estimate by Levy (1971). Concentrations of HO radical in the atmosphere depend on solar radiation and drop to nearly zero at night. Therefore we have averaged the values for daylight and dark periods to take into account this diurnal variation.

Reactions of O_3 with organic compounds are generally much slower than those involving HO•; however, the much higher concentration of O_3 (2×10^{-9} M in urban clean air) makes some reactions of O_3 competitive with those of HO radical. For the most part, however, the neglect of O_3 reactions leads to no significant error in estimates of $t_{\frac{1}{2}}$ (Darnall et al., 1976).

Rate constants for reaction of HO• (k_{HO}) in air are known with reasonable accuracy for a wide variety of organic olefins, dienes, alkanes, and aromatics (Darnall et al., 1976). However, very few data are available for more complex functionalized molecules; values measured in water are available (Anbar and Netz, 1967) for many functionalized compounds and by making some reasonable assumptions about solvent effects (Walling et al., 1974) and additivity effects of structure we have estimated values of k_{HO} and $t_{\frac{1}{2}}$ for all the compounds in Table 1 These values are listed in Table 2. Many of the values for k_{HO} are probably accurate to no more than a factor of ten. However, the

Table 2

RATE CONSTANTS AND HALF-LIVES FOR REACTION OF HO RADICAL WITH ORGANIC COMPOUNDS

Class of Compounds	Rate Constant, k_{HO} (M^{-1} s^{-1}) x 10^{-9}	Half-Life, $t_{\frac{1}{2}}$[a] (hours)
Epoxides		
All aliphatic epoxides	1.0	23
Styrene oxide and other aromatic epoxides	2.7	8.7
Haloolefins		
Chloroethylene	1.9	12
1,2-dichloroethylene	0.95	26
Trichloroethylene	0.63	36
Chlorobutadiene	23	1.1
Monochloroolefins (C_3-C_6)	8-35	0.34-3.0
Aldehydes		
Formaldehyde	9[b]	2.6
Acrolein and other aldehydes	9[b]	2.6
Dialkyl halides		
1,2-Dichloroethane	0.1	234
1,2-Dibromethane	0.1	234
Dihaloethanes (C_3-C_6)	0.3-1	23-77
Peroxides		
Di-t-butyl peroxide	0.3	79
t-butyl hydroperoxide	0.3	79
Cumyl hydroperoxide	2.7	8.5
Perpropionic acid	0.5	47
Hydrogen peroxide	1	23
Alkyl and Benzyl halides		
Benzyl chloride	2.7	8.5
Methyl chloride	0.2	117

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[a] $t_{1/2} = \ln 2/(0.8 \times 10^{-14}) k_{HO}$ daylight hours; see text.

[b] From data of Davis et al (1975).

Table 2 (continued)

RATE CONSTANTS AND HALF-LIVES FOR REACTION OF HO RADICAL WITH ORGANIC COMPOUNDS

Class of Compounds	Rate Constant, k_{HO} (M^{-1} s^{-1}) x 10^{-9}	Half-Life, $t_{\frac{1}{2}}$ (hours)
Polyhalomethanes		
Chloroform	0.5	13
Carbon tetrachloride	< 0.001	> 23400
Polychloroethanes(C_3-C_4)	0.05-1.5	16-470
Aromatic amines		
All benzidines	2	12
All biphenylamines	2	12
All naphthylamines	2	12
All anilines	2	12
Biphenyls and chlorobiphenyls		
Biphenyl	4	6
Polychlorobiphenyls	< 0.5	> 47
Azo dyes		
All azo dyes	3	7.9
Carbamates		
Ethyl carbamate	0.5	47
Hydrazines		
Hydrazine < 0.1	10[c]	2.1
Hydrazine carboxamide < 0.1	10[c]	2.1
Methyl hydrazines	> 1	> 2.1
Alkylhydrazines (C_2-C_5)	> 1	> 23

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[c] No reliable data.

Table 2 (continued)

RATE CONSTANTS AND HALF-LIVES FOR REACTION OF HO RADICAL WITH ORGANIC COMPOUNDS

Class of Compounds	Rate Constant, k_{HO} (M^{-1} s^{-1}) x 10^{-9}	Half-life, $t_{\frac{1}{2}}$ (hours)
Acyl chlorides and ketene		
Dimethylcarbamoyl chloride	0.1	230
Diethylcarbamoyl chloride	0.5	47
Benzoyl chloride	2.7	8.5
Ketene	3.8	6.4
Phosphoric acid ester		
Trimethyl phosphate	$<$ 0.1	$>$ 230
Triethyl phosphate	0.5	47
All alkyl phosphate (C_3-C_6)	1-3	6.4-23
Aziridines		
All aliphatic aziridines	0.5	47
Azirdine ethanol	0.5	47
Lactones		
Propiolactone	0.1	230
All aliphatic lactones C_4-C_{10}	0.1-3	6.4-230
Alkylsulfates		
Dimethylsulfate	0.02	1170
Diethylsulfate	0.2	117
Sultones		
All five- or six-membered sultones	0.2	117
Aryl triazenes		
All aromatic triazenes	2.7	8.5

Table 2 (concluded)

RATE CONSTANTS AND HALF-LIVES FOR REACTION OF HO RADICAL WITH ORGANIC COMPOUNDS

Class of Compounds	Rate Constant, k_{HO} $(M^{-1}\ s^{-1}) \times 10^{-9}$	Half-life, $t_{\frac{1}{2}}$ (hours)
Diazoalkanes		
Diazomethane	0.1	230
Haloalcohols		
2-Chloroethanol	0.5	47
1-Chloropropanol	0.5	47
Haloalcohols C_3-C_6	1	23
Haloethers		
Chloromethyl methyl	0.1	230
Bis(chloromethyl)	< 0.1	> 230
Bis(2-chloroethyl)	0.1	230
Hydroxylamines		
Hydroxylamine	> 0.1[b]	< 230
O- or N-ethylhydroxylamines	> 0.1[b]	< 230
Nitrosamines		
Dimethylnitrosamine	0.1	230
Diethylnitrosamine	0.5	
Alkylnitrosamines(C_3-C_6)	1-3	8.5-23
Aromatic nitrosamines	2	12
Nitrofurans		
All furans	1.0	23
Aliphatic substituted furans	3	77
Azides		
Inorganic azides not found in atmosphere except as particulate; no reliable estimate possible		

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[b] From data of Davis, et al. (1975).

reactivity of many functionalized organics toward HO· is high enough that compounds for which half-lives are predicted to be a few minutes and which are in fact several hours may still be considered as relatively nonpersistent within the framework of practical environmental assessment. As a rough rule of thumb, compounds having $k_{HO} > 1 \times 10^{9}\ M^{-1}\ s^{-1}$ have half-lives in the atmosphere of less than 12 hours and over 90% reaction in 3 days.

The reactions of alkoxy radicals (RO· where R represents any organic radical) are not important in air but might be important in the aqueous phase under some conditions. Concentrations of RO· equal to $\sim 10^{-14}$ M are anticipated for water exposed to sunlight containing oxygen and light-sensitive compounds that photodissociate (Mill and Hendry, 1976). Estimates of half-lives use this concentration. The uncertainty limits range from 1/10 to 10 times reported values. Values of k_{RO} for a wide variety of organic compounds are known and are summarized in the review of Hendry et al. (1974). Only a few compounds are reactive enough toward RO· for this process to be an important one.

Products of oxidation in the environment generally arise from one of several possible interactions of peroxy radicals ($RO_2\cdot$) with other radicals or stable molecules. We can predict qualitatively the kinds of products that will form and can make some generalizations (Mill, 1976). For example,

- Aromatic compounds will oxidize in air to give mixtures of phenols, quinones and side chain ketones, alcohols and aldehydes. In the atmosphere ring oxidation will probably dominate (> 60%) (Perry, et al., 1974; Kenley and Hendry, 1977).
- Aliphatic compounds will oxidize in air to give alcohols, ketones, alkyl nitrates, and mostly cleavage products arising from intermediate alkoxy radicals.

- Oxidations in water of both aromatic and aliphatic compounds will probably proceed through RO· and RO_2· radicals to give alcohols, ketones, and hydroperoxides (Mill et al., 1977).

Hydrolysis

Hydrolysis is an important chemical process in the aquatic environment for many compounds found in the list. The rate for hydrolysis of substrate, S, usually can be put in the form

$$-\frac{dS}{dt} = k_{obs}[S] = k_B[OH^-][S] + k_A[S][H^+] + k_N'[H_2O][S] \qquad (4)$$

where k_B, k_A and k_N are the second-order rate constants for base-catalyzed, acid-catalyzed, and neutral processes, respectively; in water $k_N'[H_2O]$ is a constant (= k_N). The pseudo-first-order rate constant, k_{obs}, is the observed rate constant for hydrolysis at constant pH. Equation (4) assumes that the individual rate processes for the acid, base, and neutral hydrolyses are each first order in substrate. With a few known exceptions, this is usually the case and

$$k_{obs} = k_B[OH^-] + k_A[H^+] + k_N \qquad (5)$$

From the autoprotolysis water equilibrium, equation (5) may be rewritten as

$$[H^+][OH^-] = K_w \qquad (6)$$

$$k_{obs} = \frac{k_B K_w}{[H^+]} + k_A[H^+] + k_N \qquad (7)$$

From equation (7) it is evident how pH affects the overall rate: at high or low pH (high OH^- or H^+) one of the first two terms is usually dominant, while at pH 7 the last term can often be most important. However, the detailed relationship of pH and rate depends on the specific values of k_B, k_A, and k_N. At any fixed pH, the overall rate process is pseudo-first order, and the half-life of the substrate is independent of its concentration and is simply

$$t_{\frac{1}{2}} = \ln 2/k_{obs} \tag{8}$$

In cases where rate constants for hydrolysis are reported only in pH regions outside those of environmental interest (pH 5-9), a value of k_{obs} and $t_{\frac{1}{2}}$ of S at pH 7 can be calculated to give a minimum rate of hydrolysis or maximum persistence. Rate constants and half-lives for most hydrolyzable compounds in this report are summarized in Table 3. Some information on hydrolysis is available only in mixed water-organic solvents or at elevated temperatures. We have relied extensively on the compilation of hydrolysis kinetic data of Mabey and Mill, (1977) to estimate persistence in aquatic systems at 25°C and pH 7.

Photochemistry

Photochemical transformations in the environment depend on absorption of photons by a compound in the uv spectrum above 290 nm, the solar cutoff. The rate of transformation depends on the efficiency of absorption of photons (the extinction coefficient), the solar irradiance, and the quantum yield. Although the chemistry of photochemical processes occurring in the environment are variable and often complex, a few generalizations are possible:

- Aromatic esters may rearrange, or undergo photohydrolysis in the presence of water; aliphatic and aromatic ketones and aldehydes will dissociate to radicals.
- Halo and nitroaromatics can photohydrolyze or be reduced in the presence of hydrocarbons (as in aqueous dispersions).

Table 3

RATE CONSTANTS AND HALF-LIVES FOR HYDROLYSIS OF ORGANIC COMPOUNDS
(25°C and pH 7)

Class/Compound	Rate Constant[a] (s^{-1})	Half-Life	Reference[b]
Epoxides			
1,2-Epoxy-			
Ethane	6.9 (-7)	12 days	
Propane	5.5 (-7)	14.6 days	
2-Methylpropane	18.3 (-7)	4.4 days	
3-Hydroxypropane	2.84 (-7)	28 days	
3-Chloropropane	9.8 (-7)	8.2 days	
3-Bromopropane	5 (-7)	16 days	
trans-2,3-Epoxy-butane	5.12 (-7)	15.7 days	
cis-2,3-Epoxy-butane	5.24 (-7)	15.3 days	
1,2-Epoxy-1-phenylethane	5.2 (-7)[c]	15 days	Audier et al.(1968)
trans-1,2-epoxy-1-phenylpropane	3.7 (-7)	21 days	Audier et al.(1968)
Aliphatic epoxides	5.7 (-7)	14 days	
Haloethers and Alcohols			
$ClCH_2OCH_3$ Chloromethyl Methylether	>90	<0.007 sec	
bis(Chloromethyl)ether	0.018	38 sec	
2-Chloroethanol	1.06 (-9)[d]	21 yr	Cowan et al.(1950)
1-Chloro-2-propanol	1.1 (-8)[d]	2 yr	Cowan et al.(1950)
Polyhalomethanes			
Dichloromethane	3.2 (-11)	704 yr	
Chloroform	6.9 (-12)	3,500 yr	

Table 3 (continued)

RATE CONSTANTS AND HALF-LIVES FOR HYDROLYSIS OF ORGANIC COMPOUNDS
(25°C and pH 7)

Class/Compound	Rate Constant[a] (s^{-1})	Half-Life	Reference[b]
Tribromomethane	3.2 (-11)	686	
Tetrachloromethane	4.8 (- 7)	7000 yr[e] 7 yr[f]	
Alkyl and benzyl halides (including 1,2-dihaloalkanes)			
Methyl chloride	1.9 (-8)	417 days	
Methyl bromide	4.0 (-7)	20 days	
Ethyl chloride	2.0 (-7)	40 days	
Ethyl bromide	1.6 (-7)	50 days	
Isopropyl chloride	2.0 (-7)	39 days	
Isopropyl bromide	3.7 (-7)	2.1 days	
t-Butyl chloride	1.0 (-4)	1.9 hr	
Benzyl chloride	1.3 (-5)	15 hr	
Benzyl bromide	1.5 (-4)	1.3 hr	
1,2-Dichloroethane	~5 (-13)	50,000 yr[g]	
1,2-Dibromoethane	~5 (-12)	5,000 yr	Buckley et al.(1967)
Carbamates and carbonates			
$EtOC(O)NH_2$ (ethyl carbamate)	20 (-12)	11,000 yr	Dittertand Higuchi (1963)
$MeOC(O)NHC_6H_5$	5.5 (-12)	4,000 yr	
$EtOC(O)N(C_6H_5)Me$	5.0 (-13)	44,000 yr	
$C_6H_5OC(O)NHC_6H_5$	5.4 (- 6)	1.5 days	

Table 3 (continued)

RATE CONSTANTS AND HALF-LIVES FOR HYDROLYSIS OF ORGANIC COMPOUNDS (25°C and pH 7)

Class/Compound	Rate Constant[a] (s^{-1})	Half-Life	Reference[b]
$C_6H_5OC(O)N(C_6H_5)Me$	4.2 (-12)	5,200 yr	
$ClCH_2CH_2OC(O)NHC_6H_5$	1.6 (-10)	140 yr	
$CCl_3CH_2OC(O)NHC_6H_5$	3.2 (- 8)	252 days	
EtOC(O)NHMe	5.7 (-13)	38,000 yr	
$EtOC(O)NMe_2$	4.5 (-13)	39,000 yr	
$C_6H_5OC(O)OEt$	2.4 (- 8)	0.9 yr	
Benzoyl and carbamoyl chlorides			
Benzoyl chloride	4.3 (-2)	16 sec	Kelly and Watson (1958)
Dimethyl carbamoyl chloride	>2.5 (-3)[h]	<4.6 min	Hall (1955)
Ethyl chloroformate	2.15(-4)[i]	53 min	Queen (1967)
Phosphoric acid esters			
Trimethyl phosphate	1.8 (-8)	1.2 yr	
Triethyl phosphate	2.2 (-9)	10 yr	
Diethyl phosphate	6.7 (-9)	3.3 yr	
Trithioethyl phosphate	2.6 (-9)	8.5 yr	
Triphenyl phosphate	1.7 (-9)	1.3 yr	
O-Ethyl-O-p-nitrophenyl-S-ethyl phosphate	2.9 (-6)	2.8 days	
O,O-Dimethyl-O-p-nitrophenyl thiophosphate (methyl parathion)	1.1 (-7)	78 days	

Table 3 (continued)

RATE CONSTANTS AND HALF-LIVES FOR HYDROLYSIS OF ORGANIC COMPOUNDS
(25^{o}C and pH 7)

Class/Compound	Rate Constant[a] (s^{-1})	Half-Life	Reference[b]
O,O-Diethyl-O-p-nitrophenyl thiophosphate (parathion)	4 (-9)	5.5 yr	
Aziridines			
Ethylenimine	5.2 (-7) (protonated)	15.4 days	Early et al.(1958); Buist and Lucas (1957)
Propylenimine	~5 (-7)	~16 days	
1-Azirideneethanol	~5 (-7)	~16 days	
Lactones			
β-Propiolactone	3.3 (-3)	3.3 hr	Long & Purchase (1950)
γ-Butyrolactone and other lactones	8 (-4)	13 hr	Long & Purchase (1950)
Alkyl sulfates and sulfonates			
Dimethyl sulfate	1.7 (-4)	1.2 hr	Robertson and Sugamori (1966)
Diethyl sulfate	1.1 (-4)	1.7 hr	Roberton and Sugamori (1966)
Ethylene sulfate	7.6 (-4)	0.25 hr	Kaiser et al. (1963)
Trimethylene sulfate	6.3 (-5)	3.1 hr	Kaiser et al. (1963)

Table 3 (concluded)

RATE CONSTANTS AND HALF-LIVES FOR HYDROLYSIS OF ORGANIC COMPOUNDS
(25°C and pH 7)

Class/Compound	Rate Constant[a] (s^{-1})	Half-Life	Reference[b]
Methylmethane sulfonate	5.0 (-7)	38 hr	Robertson and Sugamori (1966)
Ethyl benzenesulfonate	1.0 (-5)	16.5 hr	Roberton and Sugamori (1966)
Sultones			
1,3-Propane sultone	∼20 (-6)	9.6 hr	Bordwell et al. (1959)
1,4-Butane sultone	5 (-7)	16 days	
1-Aryl-3,3-dimethyl triazene[j]			
Phenyl-	5.5 (-5)	210 min	Kolar and Preusmann (1971)
P-Chlorophenyl-	4.8 (-6)	40 hr	
P-Methoxy-	1.15(-3)	10 min	
P-Nitro-	5.0 (-8)	160 days	

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[a] Numbers in parentheses are exponents of base 10.

[b] Unless otherwise stated, data are from Mabey and Mill (1977).

[c] Extrapolated from 60°C.

[d] Calculated using temperature dependent equation in Cowan et al. (1950).

[e] Concentration, 1 ppm.

[f] Concentration, 1000 ppm.

[g] Estimated to be only one tenth as reactive as dibromoethane.

[h] Measured at 3.2°C.

[i] Measured at 20°C.

[j] Measured at 37°C.

- Photooxidation is a common environmental process, but the mechanisms may involve excited states or free radicals or both, and details are very dependent on structure.

Although we have tried to estimate the importance of these processes for compounds that absorb in the solar region, the estimates are usually educated guesses made in the absence of reliable experimental data.

A reliable method for estimating the rate of a phototransformation in sunlight has been developed by Wolfe et al. (1976). This method requires only the uv spectrum for the compound and the quantum yield for the reaction. We have tried to apply the principle of this method for qualitatively estimating half-lives for some compounds for which these data are available. However, quantitative estimates require a machine computation beyond the scope of this study.

Partition Coefficients

Partition coefficients for octanol/water are often used as a reliable measure of the propensity of a compound to transfer from water to a lipid phase and bioaccumulate. The partition coefficient, log P, is defined as the log (base 10) of the ratio of the concentration in octanol to the concentration in water. Thus, log P values are directly proportional to lipophilicity or hydrophobicity as determined by equilibrium distribution of a compound between lipid and aqueous phases of a two-phase system.

However, hydrophobicity is only one measure of the tendency of a compound to bioaccumulate. Such a tendency is frequently offset by susceptibility to metabolic degradation. Metabolism generally converts lipophilic compounds to highly polar metabolites, which are readily excreted via the kidneys. Highly polar compounds are frequently excreted rapidly in unchanged form. In contrast, highly lipophilic compounds tend to pass readily into liver microsomes where drug-metabolizing enzymes are concentrated. Thus, while a high log P value tends to favor accumulation in body fat and other lipophilic tissues, it also favors rapid metabolism to easily excreted metabolites depending on the chemical constitution of the compound. In addition, continued exposure frequently stimulates such metabolism. In the absence of direct experimental data, accurate prediction of bioaccumulation potential requires knowledge of metabolic susceptibility in addition to hydrophobicity--at least in the case of highly lipophilic compounds.

Our conclusions concerning the propensity of each chemical to bioaccumulate were based primarily on their log P values (see Table 4) because in most instances, the value was the only information available. When direct experimental data were available to support or refute initial conclusions based on log P values, we included them in our discussion. When available, we also included any information on metabolism uptake and excretion, and when possible indicated how these factors might affect bioaccumulation.

Where available, measured values from the literature (Pomona College medicinal chemistry project data base) are reported. Such values have either been determined directly in an octanol/water system or calculated by applying regression equations to data obtained in other lipid/water systems. Where the data base lists several values derived by regression equations from measurements in several systems, a mean value has been calculated. A log P value of 2.0 means that distribution of a compound between oil (octanol) and water phases is such that its concentration in the oil phase is favored 100 to 1.

Table 4

PARTITION COEFFICIENTS

Class/Name	CAS Number	Log P
Epoxides		
Ethylene oxide	75-21-8	-0.30[a]
Propylene oxide	75-56-9	-0.13
Epichlorohydrin	106-89-8	0.30
Styrene oxide	96-09-3	0.98
Glycidol	556-52-5	-2.00
Glycidaldehyde	765-34-4	-1.99
Haloolefins		
Vinyl chloride	75-01-4	0.60
Trichloroethylene	79-01-6	2.29[a]
Vinylidene chloride	75-35-4	0.73
Chloroprene	126-99-8	0.57
Aldehydes		
Formaldehyde	50-00-0	-0.96[a]
Acrolein	107-02-8	-0.90
Dihaloalkanes		
1,2-Ethylene dibromide	106-93-4	1.60
1,2-Ethylene dichloride	107-06-0	1.48[a]
Polyhalomethanes		
Carbon tetrachloride	56-23-3	2.70[a]
Chloroform	67-66-3	1.92[a]

Table 4 (continued)

PARTITION COEFFICIENTS

Class/Name	CAS Number	Log P
Peroxides		
Cumene hydroperoxide	80-95-9	-0.16
Di-tert-butyl peroxide	110-05-4	0.68
Hydrogen peroxide	7722-84-1	-1.42[a]
tert-Butyl hydroperoxide	75-9-2	-1.30
Succinic acid peroxide	3504-13-0	-3.04
Alkyl halides and benzyl halides		
Benzyl chloride	100-44-7	2.30[a]
Methyl chloride	74-87-3	1.92[a]
Aromatic amines		
4,4'-Methylenebis(2-chloroaniline)	101-14-4	4.02
1-Naphthylamine	134-32-7	2.15[a]
3,3-Dichlorobenzidine	91-94-1	3.36
Benzidine	92-87-5	1.81[a]
2-Biphenylamine	90-41-5	2.10[a]
4-Biphenylamine	92-67-1	1.74[a]
4,4'-Methylenebis(2-methylaniline)	838-88-0	3.92
2-Naphthylamine	91-59-8	1.90[a]
Polychlorinated Biphenyls		
Tetrachlorobiphenyl[a]	26914-33-0	7.24
Pentachlorobiphenyl[a]	25429-29-2	8.05
Hexachlorobiphenyl[a]	59291-64-4	8.86

Table 4 (continued)

PARTITION COEFFICIENTS

Class/Name	CAS Number	Log P
Azo dyes		
Azobenzene	103-33-3	3.82[a]
4-Aminoazobenzene	60-09-3	3.50[a]
4-Dimethylaminoazobenzene	60-11-7	4.58[a]
2-Methyl-4-[(2-methylphenyl)azo]-benzenamide	97-56-3	4.25
Carbamates		
Ethyl carbamate	51-79-6	-0.75[a]
Hydrazines		
Hydrazine	302-01-2	3.08
1,1-Dimethylhydrazine	57-14-7	-1.94
Hydrazine carboxamide	57-56-7	-2.53
1,2-Dimethylhydrazine	540-73-9	-2.52
Acyl chlorides and ketene		
Benzoyl chloride	98-88-4	0.97
Diethylcarbamoyl	88-10-8	-0.12
Dimethylcarbamoyl chloride	79-44-7	-1.20
Ketene	463-51-4	b
Phosphates		
Triethyl phosphate	78-40-0	1.11[a]
Trimethyl phosphate	512-56-1	-0.52[a]

Table 4 (continued)

PARTITION COEFFICIENTS

Class/Name	CAS Number	Log P
Aziridines		
Ethylenimine	151-56-4	-1.12
1-Aziridineethanol	1072-52-2	-1.79
Propylenimine	75-55-8	-0.46
Lactones		
β-Propiolactone	57-57-8	-0.46
Sulfates		
Dimethyl sulfate	77-78-1	-4.26
Diethyl sulfate	64-67-5	-3.18
Sultones		
1,3-Propane sultone	1120-71-4	-2.82
1,4-Butane sultone	1633-83-6	-2.45
Aryl dimethyltriazenes		
3,3-Dimethyl-1-phenyltriazene	7227-91-0	2.59[a]
1-(p-Chlorophenyl)-3,3-dimethyltriazene	7203-90-9	3.00[c]
Diazoalkanes		
Diazomethane	334-88-3	b
Chloroalcohols and Ethers		
2-Chloroethanol	107-09-3	0.03[a]
1-Chloropropanol	127-00-4	-0.06
Chloromethylmethyl ether	107-30-2	-0.21

Table 4 (concluded)

PARTITION COEFFICIENTS

Class/Name	CAS Number	Log P
Bis(2-chloroethyl)ether	11-44-4	0.70
Bis(chloroethyl)ether	542-88-1	-0.38
Hydroxylamine		
Hydroxylamine	7803-49-8	-3.18
N-Methylhydroxylamine	593-77-1	-2.90
O-methylhydroxylamine	67-62-0	-2.47
Nitrosoamines		
N-Nitrosodimethylamine	62-75-9	0.06
N-Nitrosodiethylamine	55-18-5	1.14
Furans		
2-Nitrofuran	609-39-2	1.86
N-[4-(5-nitro-2-furanyl)-2-thiazolyl]-acetamide	531-82-8	-0.60
N-[4-(5-nitro-2-furanyl)-2-thiazolyl]-formamide	24554-26-5	-1.14
Azides		
Sodium azide	26628-22-8	b

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[a] Literature values; all others are calculated.

[b] Insufficient data available; these are reactive, polar compounds with expected log P <1.0.

[c] Literature value is for the o-chloro isomer.

When no literature data were available, log P was calculated either from a parent solute and the known additive π constants for substituents (Hansch et al., 1973; Leo et al., 1971) as shown by Equation (9):

$$\log P_{RX} = \text{Log } P_{RH} + \pi_X \qquad (9)$$

or by summation of fragmental constants (f; assembly of the solute from its component parts) (Nys et al., 1973; Leo, 1976) as represented by Equation (10):

$$\log P = \sum_{1}^{n} a_n f_n \qquad (10)$$

Either method yields reasonably reliable estimates of lipophilicity within a log P range of more than 10^8 (less than -1.0 to more than + 7.0).

4. EPOXIDES

Production and Properties

Ethylene oxide is produced in the highest quantities of the chemicals in this group. Production estimates are given below (in pounds per year):

Ethylene oxide	3893 million	(1974)
Propylene oxide	1756 million	(1974)
Epichlorohydrin	180 million	(1973)
Styrene oxide	>1000	(1974)
Glycidol	>1000	(1974)
Glycidaldehyde	<1000	(1974)

Producers and locations are given in Table 5. Table 6 lists the synonyms for chemical in this group and some of their physical and chemical properties.

Table 5

PRODUCERS AND LOCATIONS FOR EPOXIDES

Compound	Producers	Site
Ethylene oxide	BASF Wyandotte Corp.	Geismar, Louisiana
	Cacasiu Chemical Corp.	Lake Charles, Louisiana
	Celanese Chemical Co.	Clear Lake, Texas
	Dow Chemical Co.	Freeport, Texas
		Plaquemine, Louisiana
	Jefferson Chemical Co.	Port Neches, Texas
	Northern Petrochemical Co.	East Morris, Illinois
	Olin Corp.	Brandenburg, Kentucky
	Oxirane Corp.	Channelview, Texas
	PPG Industries	Beaumont, Texas
		Guayanella, Puerto Rico
	Shell Chemical Co.	Geismar, Louisiana
	Sunolin Chemical Co.	Claymont, Delaware
	Texas Eastman Co.	Longview, Texas
	Union Carbide Corp.	Seadrift, Texas
		Taft, Louisiana
		Texas City, Texas
		Ponce, Puerto Rico

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Table 5 (Concluded)

PRODUCERS AND LOCATIONS FOR EPOXIDES

Compound	Producers	Site
Propylene oxide	BASF Wyandotte Corp.	Wyandotte, Michigan
	Dow Chemical Co.	Freeport, Texas Plaquemine, Louisiana
	Jefferson Chemical Co.	Port Neches, Texas
	Olin Corp.	Brandenburg, Texas
	Oxirane Corp.	Bayport, Texas Channelview, Texas
Epichlorohydrin	Dow Chemical Co.	Freeport, Texas
	Shell Chemical Co.	Deer Park, Texas Norco, Louisiana
Styrene oxide	Union Carbide Corp.	Taft, Louisiana
Glycidol	Dixie Chemical Co.	Bayport, Texas
	FMC Corp.	Bayport, Texas

Table 6

PHYSICAL AND CHEMICAL PROPERTIES OF EPOXIDES

Compound, Synonyms	Mol. wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ_{max} (log ϵ)	Solubility
Ethylene oxide; oxirane; dihydrooxirene; dimethylene oxide; 1,2-epoxyethane.	44.05	-111	-13.5^{746}	0.8824_{10}^{10}	1.3597^{7}	(gas) 169(3.58) 171(3.57)	Soluble in water, alcohol, ether, acetone, and benzene
Propylene oxide; methyloxirane; 1,2-epoxypropane; propene oxide.	58.08		34.3	0.859_4^0	1.3670^{20}		Infinitely soluble in water, alcohol and ether
Epichlorohydrin; 1-chloro-2,3-epoxypropane; chloromethyloxirane; chloropropylene oxide; α-epichlorohydrin	92.53	-48	116.5^{760} $60\text{-}1^{100}$	1.1801_4^{20}	1.4361^{20}		Slightly soluble in cold water, decomposes in hot water, infinitely soluble in alcohol and ether, soluble in benzene
Styrene oxide; phenyloxirane; 1,2-epoxyethylbenzene	120.16		194.1 $84\text{-}5^{15}$	1.0523_4^{16}	1.5342^{20}	250sh (2.2),254 (2.24),260 (2.28),265sh (2.10)in alcohol	Insoluble in water, soluble in alcohol and ether
Glycidol; 2,3-epoxy-1--propanol; oxiranemethanol; glycidyl alcohol; 3-hydroxy-1,2-epoxy-propane	74.08		56.5^{11}	1.117_4^{20}	1.4293^{16}		Soluble in water, alcohol, ether, acetone, chloroform, and benzene

Environmental Transformation

Lower aliphatic epoxides such as ethylene or propylene oxides are volatile polar compounds that are moderately reactive toward a variety of nucleophilic species including water via acid, base, and neutral reactions. In general, structure has little effect on the rates of hydrolysis of terminal epoxides to diols by neutral water. For example, aliphatic terminal epoxides have half-lives of 338 ± 200 hours at 25°C; aromatic substituents such as phenyl or benzyl show this same reactivity pattern. Data for hydrolysis of a number of epoxides are summarized in Table 3.

A more detailed analysis of the rate data indicate that more heavily substituted epoxides (such as isobutylene oxide) probably hydrolyze mostly by a fast acid-catalyzed process; in acidic waters (pH 5-6) these epoxides would have half-lives of less than 100 hours.

No photochemical processes are important for simple aliphatic epoxides; however, aromatic epoxides that absorb in the solar region probably undergo photohydrolysis in water and this could significantly reduce the half-life (Hisaoka and Tokumara, 1973). Biodegradation may be an important competing process for many epoxides, but oxidation in water is probably very slow.

If dispersed into the atmosphere, epoxides would be oxidized by HO radical with half-lives of 3 to 11 hours. Products of oxidation probably include formic esters, CO, CO_2, and oxidized aliphatic fragments. Glycidaldehyde would probably photolyse via the aldehyde chromosphere at about the same rate as oxidation. Washout by rain is likely to be important only for low molecular weight epoxides.

Bioaccumulation

The log P values for ethylene oxide, propylene oxide, glycidol, glycidaldehyde, and epichlorhydrin are negative (see Table 4). Only styrene oxide has a positive log P value (0.98). We believe that none of these compounds will accumulate significantly in animal tissues.

In vitro studies by James and White (1967) and by James et al. (1976) have shown that styrene oxide is metabolized by the liver of rats and rabbits and that the reaction is catalyzed by microsomal epoxide hydrase and by glutathione-s-epoxide transferase. These studies do not reflect the rate or extent of styrene oxide metabolism in vivo. If there are enzymes that act on all the epoxides studied, metabolism of a compound could reduce the extent of accumulation.

5. HALOOLEFINS

Production and Properties

All the compounds in this category are commercially important. The estimated production figures are given below (in millions of pounds per year):

Vinyl chloride	5621	(1974)
Trichloroethylene	338	(1974)
Chloroprene	349	(1975)
Vinylidene chloride	60	(1972)

Producers and locations are given in Table 7, and chemical and physical properties are listed in Table 8.

Table 7

PRODUCERS AND LOCATIONS FOR HALOOLEFINS

Compound	Producer	Site
Vinyl chloride	Allied Chemical Corp.	Baton Rouge, Louisiana
	Borden, Inc.	Geismar, Louisiana
	Continental Oil Co.	Westlake, Louisiana
	Diamond Shamrock	LaPorte, Texas
	Dow Chemical Co.	Freeport, Louisiana Midland, Michigan Oyster Creek, Texas Plaquemine, Louisiana
	Ethyl Corp.	Baton Rouge, Louisiana Pasadena, Texas
	B. F. Goodrich Co.	Calvert City, Kentucky
	Monochem, Inc.	Geismar, Louisiana
	PPG Industries	Lake Charles, Louisiana Guayanilla, Puerto Rico
	Shell Chemical Co.	Deer Park, Texas Norco, Louisiana
	Stauffer Chemical Co.	Carson, California

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Table 7 (Concluded)

PRODUCERS AND LOCATIONS FOR HALOOLEFINS

Compound	Producer	Site
Trichlorethylene	Diamond Shamrock Corp.	Deer Park, Texas
	Dow Chemical Co.	Freeport, Texas
	Ethyl Corp.	Baton Rouge, Louisiana
	Occidental Petroleum Corp.	Taft, Louisiana
	PPG Industries	Lake Charles, Louisiana
Chloroprene	Dow Chemical Co.	Freeport, Texas
	Shell Chemical Co.	Deer Park, Texas Norco, Louisiana
Vinylidene chloride	Dow Chemical Co.	Freeport, Texas Plaquemine, Louisiana
	PPG Industries	Lake Charles, Louisiana

Table 8

PHYSICAL AND CHEMICAL PROPERTIES OF HALOOLEFINS

Compound, Synonyms	Mol. wt.	M.P. °C	B.P. °C	Density	n_D	λ_{max} (log ε)	Solubility
Vinyl chloride; chloroethylene; chloroethene;	62.50	-153.8	-13.37^{760}	0.9106^{20}_{4}	1.3700^{20}		Slightly soluble in water, soluble in alcohol, very soluble in ether
Trichloroethylene; trichloroethene;	131.39	-73	87^{760}	1.4642^{20}_{2}	1.4773^{20}	<200 (vapor)	Slightly soluble in water, infinitely soluble in alcohol and ether, soluble in chloroform and acetone
Chloroprene; 2-chloro-1,3-butadiene	88.54		59.4^{760} 6.4^{100}	0.9583^{20}_{4}	1.4583^{20}_{4}	223(4.15) (hexane)	Slightly soluble in water, infinitely soluble in ether, acetone, benzene, and other organic solvents
Vinylidene chloride; 1,1-dichloroethylene; 1,1-dichloroethene;	96.94	-122.1	37^{760}	1.218^{20}	1.4249^{20}	<200 (vapor)	Insoluble in water, soluble in alcohol, acetone, and benzene, very soluble in chloroform and ether.

Environmental Transformation

In water, oxidation of haloolefins by RO radical and hydrolysis of vinylic halides will be extremely slow with half-lives of more than 20 years (Hill et al., 1976). Unless biodegradation is very rapid, the most likely fate of haloolefins is bioaccumulation or volatilization to the atmosphere and oxidation.

The relatively low solubility and high volatility of most low molecular weight chloroolefins will promote their rapid transfer to the atmosphere, where we estimate that half-lives toward HO radical are less than 50 hours; for conjugated olefins such as chlorobutadienes the half-life will be much less than 10 hours. Products formed by oxidation of these compounds are predicted to be $COCl_2$, HCl, and CO with likelihood of formation of CH_2O as well. Most simple and conjugated haloolefins will also oxidize to lower molecular weight acids (Mill and Hendry, 1976). Oxidation of perhaloolefins by oxygen is a rapid process with neat substrate but exhibits exceptional sensitivity to inhibitors (Mayo, 1965). In natural waters we would not expect this process to be very important.

Bioaccumulation

Based on its log P value and some experimental evidence, vinyl chloride should not accumulate appreciably in animals. We found no experimental data demonstrating whether vinylidene chloride and chloroprene do or do not accumulate; however, their log P values suggest that they should not. Trichloroethylene has a high log P value, and experimental evidence indicates that it may bioaccumulate.

Our calculated log P value for vinyl chloride is 0.60, which indicates that it is slightly lipophilic; however, its affinity for lipid material is too low to expect significant bioaccumulation. Green and Hathaway (1975) reported that in rats, the main route of excretion of vinyl chloride after oral, i.v., or i.p. administration is pulmonary. Excretion is rapid and the percentage of the dose excreted increases with the dose. The amount excreted through the lungs may be as high as 99% in 24 hours. Chronic administration (60 days) of vinyl chloride did not affect elimination of a single dose of ^{14}C-labeled vinyl chloride. These investigators also studied the metabolism of vinyl chloride and have devised a metabolic scheme for the compound.

Hefner et al. (1975) determined the amount of radioactivity in 12 tissues, including fat, from rats exposed to ^{14}C-vinyl chloride for up to 2.5 hours. They found radioactivity only in the liver, bile, and kidney.

Vinylidene chloride is slightly more lipophilic than vinyl chloride, having a calculated log P value of 0.73. Like vinyl chloride, it should not accumulate significantly in animals. Although we found considerable information about its toxicity, we did not find any information pertinent to bioaccumulation.

The experimentally determined log P value for trichloroethylene is 2.29, which indicates that it may bioaccumulate.

Cohen and coworkers (1958, cited in Walter et al., 1976) reported detectable levels of trichloroethylene in the blood, brain, adrenals, fat, heart, kidney, liver, lung, muscle, pancreas, spinal cord, cerebral spinal fluid, spleen, and thyroid of animals exposed to the compound for periods up to 219 hours. The relative amounts of trichloroethylene in these tissues were not reported in the secondary source because the data were not adequate for determining the relationship of the concentration in the tissues. We found no other reference to the distribution of the compound in different tissues and therefore cannot verify the bioaccumulating potential suggested by the partition coefficient.

According to Stewart and coworkers (1962), trichloroethylene appears in the blood of humans about 30 minutes after the beginning of exposure. After cessation of exposure, the blood concentration rapidly diminishes. Pfaffli and Backman (1972) also observed a rapid reduction of trichloroethylene in human blood after cessation of exposure; however, they found detectable levels in the blood and expired air up to 15 hours after exposure was stopped. Stewart and coworkers (1970) observed that in humans urinary excretion of trichloroacetic acid, a biotransformation product of trichloroethylene, increased progressively after cessation of exposure and reached a peak after five days. These studies suggest that after absorption, trichloroethylene is partly stored in tissues and released slowly to be excreted unchanged or as biotransformation products. It is conceivable that repeated exposure would lead to a buildup of the compound in tissues.

Chloroprene has a calculated log P value of 0.57, which indicates that it has a low propensity to bioaccumulate. We did not find any information on its fate, distribution, or retention in animals.

6. ALDEHYDES

Production and Properties

Formaldehyde is a very important material commercially, and acrolein is produced in appreciable quantities, but only in about one hundredth the amount of formaldehyde. Estimated production (in millions of pounds per year) is:

Formaldehyde	5765	(1974)
Acrolein	61	(1974)

Sources for formaldehyde are quite extensive and are not limited to any one area of the country. Producers and locations are given in Table 9. Synonyms and physical and chemical properties are given in Table 10.

Table 9

PRODUCERS AND LOCATIONS FOR ALDEHYDES

Product	Producer	Location
Formaldehyde	Allied Chemical Co.	South Point, Ohio
	Borden, Inc.	Demopolis, Alabama
		Deboll, Texas
		Fayetteville, N. Carolina
		Geisma, Louisiana
		Louisville, Kentucky
		Sheboygan, Wisconsin
		Fremont, California
		Kent, Washington
		LaGrande, Oregon
		Missoula, Montana
		Springfield, Oregon
	Celanese Corp.	Bishop, Texas
		Newark, New Jersey
		Rock Hill, S. Carolina
	E.I. du Pont de Nemours and Co., Inc.	Belle, W. Virginia
		La Porte, Texas
		Healings Springs, N. Carolina

Table 9 (Continued)

PRODUCERS AND LOCATIONS FOR ALDEHYDES

Product	Producer	Location
	E.I. du Pont de Nemours (continued)	Linden, New Jersey
		Toledo, Ohio
	G A F Corp.	Calvert City, Kentucky
	Georgia-Pacific Corp.	Albany, Oregon
		Columbus, Ohio
		Coos Bay, Oregon
		Crossett, Arkansas
		Russellville, S. Carolina
		Taylorsville, Mississippi
		Vienna, Georgia
	Gulf Oil Corp.	Vicksburg, Mississippi
	Hercules, Inc.	Louisiana, Missouri
	International Minerals and Chemical Corp.	Wilmington, N. Carolina
		Seiple, Pennsylvania
		Sterlington, Louisiana
	Monsanto Co.	Addyston, Ohio
		Chocolate Bayou, Texas
		Eugene, Oregon
	Occidental Petroleum Corp.	North Tonawanda, New York
	Reichhold Chemicals, Inc.	Hampton, S. Carolina
		Kansas City, Kansas
		Houston, Texas
		Malvern, Arkansas
		Moncure, N. Carolina
		Tacoma, Washington
		Tuscaloosa, Alabama
	Rohm and Haas Co.	Philadelphia, Pennsylvania
	Skelly Oil Co.	Springfield, Oregon
		Winnfield, Louisiana
	Tenneco Inc.	Fords, New Jersey
		Garfield, New Jersey
	Union Carbide	Bound Brook, New Jersey
	Univar Corp.	Eugene, Oregon
	Wright Chemical Corp.	Acme, N. Carolina
Acrolein	Shell Chemical Co.	Norco, Louisiana
	Union Carbide Corp.	Taft, Louisiana

Table 10

PHYSICAL AND CHEMICAL PROPERTIES OF ALDEHYDES

Compound	Mol. Wt.	M.P. °C	B.P. °C	Density	n_D	λ_{max} (log ϵ)	Solubility
Formaldehyde; formalin, methanal; oxomethane, oxymethylene	30.03	-92	-21^{760} -79.6^{20}	0.815_4^{-20}		155(4.37) 175(4.26) (vapor)	Soluble in water, alcohol, and chloroform; infinitely soluble in ether, acetone, and benzene
Acrolein; 2-propenal; acryladehyde; allyl aldehyde	56.07	-36.95	52.5-53.5	0.8410_4^{20}	1.4017^{20}	207(4.05) in alcohol	Very soluble in water, soluble in alcohol, ether, and acetone

Environmental Transformation

Formaldehyde is almost entirely hydrated in water. It is nonvolatile and is inactive toward photochemical dissociation. Higher aldehydes are less hydrated, more volatile, and absorb weakly in the solar region dissociating to RCO and H atoms, followed by oxidation to peroxides and cleavage products (Calvert and Pitts, 1966). Oxidation by RO radical in water may be fairly rapid to give similar products. Acrolein would be expected to oxidize at the double bond to give keto aldehydes and cleavage products. Biotransformation of many aldehydes in water would be expected to be an important competing process for which we have no reliable data. In general, neither the aldehydes nor their oxidation products would be expected to be persistent in water.

In air aldehydes are expected to photodissociate to RCO and H atoms rapidly and competitively with their oxidation by HO radical, for a half-life of 2 to 3 hours (Calvert and Pitts, 1966; Hendry, 1977). In chamber studies NO_2 accelerates this process (Bufalini et al., 1972). The photochemical process would lead to peracylnitrates and peroxy radicals that would enter the photochemical cycle. Oxidation by HO• would give the same products, to the extent that HO• removes the aldehydic H atom, but also could give oxidation of the alkyl chain in higher aldehydes, phenol from aromatic aldehydes, and addition to acrolein's double bond. Aldehydes will not persist in the atmosphere, but their contribution to smog may be significant (Hendry, 1977).

Bioaccumulation

Neither formaldehyde nor acrolein shows a tendency to bioaccumulate. Their calculated log P values are similar and negative. Formaldehyde is a normal product of metabolism and is rapidly metabolized to formic acid and carbon dioxide. We found little information on acrolein and none of it was pertinent.

Formaldehyde reacts rapidly with tissues to cause crosslinking and precipitation of proteins. Upon entering the bloodstream, it disappears rapidly by reactions with body tissues and by oxidation to formic acid (Kitchens et al., 1976). It is a natural metabolic product that plays an important role in the one-carbon pool (Koivusalo, 1956, 1970). Its experimentally determined log P value of -0.96 suggests that it should not bioaccumulate.

The calculated log P value for acrolein is -.090; hence accumulation in tissues should be negligible.

7. ALKYL AND BENZYL HALIDES

Production and Properties

Alkyl halides such as methyl chloride and ethylene dichloride are produced in large quantities for use in the production of Freons, vinyl chloride, and trichloroethylene. Both ethylene dichloride and ethylene dibromide are used as scavenging agents in gasoline and as fumigants. Estimated production (in millions of pounds per year) is as follows:

1,2-Ethylene dichloride	9165	(1974)
1,2-Ethylene dibromide	332	(1974)
Methyl chloride	647	(1974)

Producers and locations are given in Table 11. Synonyms and the physical and chemical properties are listed in Table 12.

Benzyl chloride's principal use is as an intermediate in the synthesis of other materials. Estimated production was 100 million pounds per year in 1976. Producers and plant locations are given below.

Benzyl chloride	Monsanto Co.	Bridgeport, New Jersey
	Stauffer Chemical Co.	Edison, New Jersey
	Tenneco Chemicals	Fords, New Jersey

Synonyms and the physical and chemical properties of benzyl chloride are also listed in Table 12.

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Table 11

PRODUCERS AND LOCATIONS FOR ALKYL HALIDES

Compound	Producer	Location
1,2-Ethylene dichloride	Allied Chemical Co.	Baton Rouge, Louisiana
	Continental Oil Co.	Westlake, Louisiana
	Diamond Shamrock	Deer Park, Texas
	Dow Chemical Co.	Freeport, Texas Oyster Creek, Texas Plaquemine, Louisiana
	Ethyl Corp.	Baton Rouge, Louisiana
	B.F. Goodrich Co.	Calvert City, Kentucky
	PPG Industries	Lake Charles, Louisiana Guayanilla, Puerto Rico
	Shell Chemical Co.	Deer Park, Texas Norco, Louisiana
	Stauffer Chemical Co.	Carson, California
	Union Carbide Corp.	Taft, Louisiana Texas City, Texas
	Vulcan Materials Co.	Geisma, Louisiana
1,2-Ethylene dibromide	Dow Chemical Co.	Magnolia, Arkansas Midland, Michigan
	Ethyl Corp.	Magnolia, Arkansas
	Great Lakes Chemical Corp.	El Dorado, Arkansas
	PPG Industries	Beaumont, Texas
Methyl Chloride	Allied Chemical Co.	Moundsville, W. Virginia
	Continental Oil Co.	Westlake, Louisiana
	Diamond Shamrock	Belle, W. Virginia
	Dow Chemical Co.	Freeport, Texas Plaquemine, Louisiana
	Dow Corning Corp.	Carrollton, Kentucky Midland, Michigan
	E.I. du Pont de Nemours and Co., Inc.	Niagara Falls, New York
	Ethyl Corp.	Baton Rouge, Louisiana
	General Electric Co.	Waterford, New York
	Stauffer Chemical Co.	Louisville, Kentucky
	Union Carbide Corp.	Institute and South Charleston, W. Virginia
	Vulcan Materials Co.	Newark, New Jersey

Table 12

PHYSICAL AND CHEMICAL PROPERTIES OF ALKYL AND BENZYL HALIDES

Compound, Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	Solubility
1,2-Ethylene dichloride	98.96	-35.36	83.47^{760}	1.2351^{20}	1.4448^{20}	Slightly soluble in water; soluble in acetone, chloroform, benzene, and organic solvents; very soluble in alcohol; infinitely soluble in either
1,2-Ethylene dibromide 1,2-Dibromoethane; Freon 150	187.87	9.79	131.36^{760} 29.1^{10}	2.1792^{20}_{4}	1.5387^{20}	Slightly soluble in water; soluble in acetone, benzene; very soluble in alcohol; infinitely soluble in ether.
Methyl chloride; chloromethane	50.49	-97	-23.76^{760}	0.92^{20}	1.3661^{-10}	Soluble in water and alcohol; infinitely soluble in ether and chloroform

Table 12 (Concluded)

PHYSICAL AND CHEMICAL PROPERTIES OF ALKYL AND BENZYL HALIDES

Compound, Synonyms	Mol. Wt.	M.P. (^{o}C)	B.P. (^{o}C)	Density	n_D	Solubility
α-Chlorotoluene; (chloromethyl) benzene; tolyl chloride[a]	126.56	-39	179.3^{760}	1.1002^{20}	1.5391^{20}	Insoluble in water; infinitely soluble in alcohol, ether, and chloroform

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[a] λ_{max} (log ϵ) = 217 (3.85) in alcohol.

Environmental Transformation

Low molecular weight alkyl halides through butyl or pentyl halides are relatively insoluble, volatile, and unreactive. Thus transfer to the atmosphere from water or soil is a likely competitive environmental process. Reliable rate constants for hydrolysis of many alkyl halides are available and a number of values are given in Table 3. Methyl chloride is persistent with a half-life (hydrolysis) of over one year. Most other simple alkyl halides are much more reactive with half-lives of 50 days or less. Benzyl halides are very reactive with half-lives of a few minutes. Vicinal (1,2-dihalo) dihalides and hydroxyalkyl halides are unreactive in water.

The hydrolysis data suggest the following generalizations about RX:

- The rate of hydrolysis is greatest when X is Br, least when X is F. Br is more reactive than Cl by a factor of 5 to 10.
- Rate of hydrolysis increases as R changes from primary to secondary to tertiary in the ratio 1:1:1000 for Cl and 1:20 for Br.
- Allylic groups enhance the rate of hydrolysis of primary halides by a factor of 5 to 100; benzyl groups enhance the rate by a factor of 50.
- Geminal (1,1-dihalo) dihalides and 2-hydroxyalkyl halides are about one-thousandth as reactive as the simple alkyl halides.

Oxidation of alkyl halides in water by RO radical is not significant ($t_{1/2} > 100$ years). However oxidation in the atmosphere should be relatively rapid, $t_{1/2} < 20$ hours, for most alkyl halides to give acid halides and halogenated ketones and aldehydes.

Benzyl halides will be more reactive toward HO· than alkyl halides by a factor of 3 to 10 and give mostly phenols, e.g., chloromethylphenol from benzyl chloride (Kenley and Hendry, 1977).

Bioaccumulation

Methylene dichloride, ethylene dibromide, and methyl chloride are slightly lipophilic. Log P values for these compounds range from 1.48 to 1.92, indicating that these compounds have a slight tendancy to accumulate in fatty tissue. However, experimental evidence indicates, at least for methylene and ethylene dichloride, that these compounds do not accumulate in lipids.

The experimentally determined value of log P for ethylene dichloride is 1.48, which indicates that it is slightly lipophilic, thus has a slight tendency to bioaccumulate. We believe that bioaccumulation would be minimal. The compound is rapidly excreted mostly unchanged in the urine of mice, with about 95% excreted in 24 hours (Yllner, 1971). Ethylene dichloride is metabolized (Heppel and Porterfield, 1948; Bray et al., 1952; Van Dyke and Wineman, 1971; Yllner, 1971). Enzymatic dechlorination has been observed in *in vitro* systems; however, in intact animals, Yllner (1971) found that the compound is metabolized to monochloroacetic acid through 2-chloroethanal with liberation of carbon dioxide.

The calculated log P value for ethylene dibromide is 1.60, indicating that it is slightly lipophilic and may have a slight tendency to accumulate. Johns (1976) reported that Lauze (1922) obtained data indicating a mild tendency of ethylene dibromide to accumulate in the liver and brain of unspecified laboratory animals. He found that the compound is excreted unchanged by the lungs and is partially decomposed in the body, producing bromide that appears in the urine.

A more recent study (Plotnick and Conner, 1976) using radiotracer techniques, showed that ethylene dibromide, administered intraperitoneally in guinea pigs, distributed itself throughout the body and concentrated primarily in the kidneys, liver, and adrenals. The kidney and liver contained the highest percentage of the injected dose, which is not surprising because the study showed that the kidney was the major route of excretion and the liver is usually the organ that metabolizes or detoxifies foriegn chemicals. Only a small amount of the administered dose was found in fatty tissue.

We found no information concerning bioaccumulation for methyl chloride. The experimentally determined log P value for this compound is 1.92, which is higher than the values for methylene dichloride and ethylene dichloride, but in the same order of magnitude. Although its log P value indicates that it has a slight affinity for lipids, we do not expect it to bioaccumulate significantly.

α - Chlorotoluene is lipophilic as indicated by its experimentally determined log P value of 2.30. We found no other pertinent information on this compound.

8. PEROXIDES, HYDROPEROXIDES, PERACIDS, AND HYDROGEN PEROXIDE

Production and Properties

Organic peroxides are used in a broad spectrum of commercial and laboratory polymerization reactions. Estimated production figures for the commercially more important peroxides are given below (in pounds per year).

Cumene hydroperoxide	3062 million	(1974)
Di-tert-butyl peroxide	3 million	(1974)
Hydrogen peroxide	1.9 million	(1974)
tert-butyl hydroperoxide	>1000	(1974)
Succinic acid peroxide	>1000	(1974)

Producers and sites are given in Table 13. Table 14 lists the synonyms and chemical and physical properties of the peroxides.

Table 13

PRODUCERS AND LOCATIONS FOR PEROXIDES

Compound	Producer	Location
Cumene hydroperoxide	Allied Chemcial Corp.	Frankford, Pennsylvania
	Hercules, Inc.	Gibbstown, New Jersey
	Pennwalt Corp.	Genesco, New York
	Reichhold Chems., Inc.	Austin, Texas
Di-tert-butyl peroxide	Akzona, Inc.	Burt, New York
	Dart Industries, Inc.	Elyria, Ohio
	The Norac Co., Inc.	Azusa, California
	Pennwalt Corp.	Crosby, Texas
	Reichhold Chemicals, Inc.	Austin, Texas
	Shell Chemical Co.	Martinez, California
	Witco Chemical Corp.	Marshall, Texas
Hydrogen peroxide	Allied Chemical Co.	Syracuse, New York
	Barium & Chemicals, Inc.	Steubenville, Ohio
	E.I. du Pont de Nemours	Memphis, Tennessee
	FMC Corp.	S. Charleston, W. Virginia
		Vancouver, Washington
	Pennwalt Corp.	Wyandotte, Michigan
	PPG Industries	Barberton, Ohio
	Shell Chemical Co.	Norco, Louisiana

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Table 13 (Concluded)

Compound	Producer	Location
tert-Butyl hydroperoxide	Akzona Inc.	Burt, New York
	Dart Industries, Inc.	Elyria, Ohio
	The Norac Co., Inc.	Azusa, California
	Oxirane Corp.	Bayport, Texas
	Pennwalt Corp.	Genesco, New York
	Witco Chemical Corp.	Marshall, Texas

Table 14

PHYSICAL AND CHEMICAL PROPERTIES OF PEROXIDES

Compound, Synonyms	Mol. wt.	M.P. (^{o}C)	B.P. (^{o}C)	Density	^{n}D	Solubility
Di-tert-butyl peroxide; Bis(1,1-dimethylethyl) peroxide; tert-butyl peroxide	146.23	-40	111^{760} 70^{197}	0.794^{20}	1.3890^{20}	Insoluble in water, soluble in organic solvents, infinitely soluble in acetone
Hydrogen peroxide; hydrogen dioxide	34.02	-0.43	152	1.463^{0}		Mixible with water; soluble in ether; decomposed by many organic solvents.
tert-Butyl hydro peroxide; 1,1-dimethyl-ether hydroperoxide	90.12	-8	35^{20}	0.896^{20}_{4}	$1,4007^{20}_{4}$	Soluble in organic solvents

Environmental Transformation

Di-t-alkylperoxides such as di-t-butyl peroxide are only slightly volatile but moderately soluble in water and therefore are most likely to remain in aquatic systems. Contrary to common belief, tertiary peroxides are thermally stable to at least 60°C and not very susceptible to trace metal ion catalysis. These peroxides have weak tailing absorbance in the solar spectrum, which leads to O-O bond cleavage to give RO radicals, which cleave to ketones and R• radicals (Calvert and Pitts, 1966). This process will be slow: we estimate $t_{1/2} > 20$ hours. Neither hydrolysis nor oxidation by RO radical is likely to be competitive with photochemistry in aquatic systems. The same photochemical process will occur in the atmosphere at a somewhat higher rate (no cage return of radicals) and compete with oxidation by HO radical, which is relatively slow.

Hydroperoxides, peracids, and hydrogen peroxide are all more polar, less volatile, and more reactive than the dialkyl peroxides because of the relatively weak and polar O-H bond that makes peroxides susceptible to radical reactions as well as to reactions with metal ions and light. The presence of Fe^{2+} and Mn^{2+} in aquatic systems in catalytically significant amounts (> 1 ppm) suggests that these peroxides will decompose rapidly ($t_{1/2} < 10$ hours) by reactions with metal ions to give alcohols, acids, or water (depending on the starting peroxide) (Hiatt et al., 1968).

Photochemical and HO radical oxidation are likely pathways for transformation of peroxides in the atmosphere. We estimate that half-lives will be less than a few hours. As an added source of free radicals, peroxides will contribute to buildup of photochemical smog.

Reliable data on the rates of radical reactions and metal catalyzed reactions of peroxides in water are lacking. Some recent data indicates that such reactions may be appreciably different in rate from those measured in organic solvents (Hiatt, 1977).

Bioaccumulation

Out literature search indicated that little is known about the fate and distribution of these five peroxides in animals. Their log P values are less than 1, which indicates that none shows a potential to bioaccumulate in intact form, i.e., without reacting chemically with biological constituents.

Much has been published on the role of hydrogen peroxide in metabolism. It is a normal metabolite in both plants and animals (Halliwell, 1974; Thurman et al., 1975; Hildebrandt et al., 1973; Chumakov and Smelyanskaya, 1974). Since the experimentally determined log P value for hydrogen peroxide is -1.42, bioaccumulation should not occur.

We did not find any pertinent information on bis(dimethylethyl) peroxide. Of the five peroxides investigated, it has the highest log P value (0.68); however, its affinity for lipids is too low to expect significant accumulation in animals.

Tertiary butyl hydroperoxide has a calculated log P value of -1.30 and should therefore not bioaccumulate. In vitro studies with rats indicate that the compound is reduced specifically by glutathione peroxidase in erythrocytes. (Sies, 1972).

No pertinent information on cumene hydroperoxide was found. It has a calculated log P value of -0.16 and therefore should not bioaccumulate.

Succinic monoperoxy acid is strongly lipopholic, having a calculated log P value of -3.04. Accumulation of this compound in animals is not expected.

9. POLYHALOMETHANES

Production and Properties

Polyhalomethane uses range from solvents and grain fumigants to intermediates and fire extinguishants. Production estimates (in millions of pounds per year) for 1974 were:

Carbon tetrachloride	1,600
Chloroform	300

Producers and locations are given in Table 15. Synonyms and physical and chemical properties are given in Table 16.

Environmental Transformation

Carbon tetrachloride is predicted to have a half-life of about 7,000 years in aquatic systems at 1 ppm; in the atmosphere where the great bulk of CCl_4 is found, the half-life in the troposphere is at least 10 years. Indeed, recent detailed analyses of the distribution of CCl_4 in the environment indicate that most of what has been produced in the past 60 years is still mostly in the atmosphere with lesser amounts in soil and water. No natural sources of CCl_4 have been identified; nor are any needed to account for its present environmental burden (Singh et al., 1976).

Other polyhalomethanes including $CHCl_3$, $CHBr_3$, and CH_2Cl_2 are only slightly more reactive in water but much more reactive in the atmosphere. Hydrolyses of these compounds in water have half-lives of about 3500 and 700 years, respectively. Oxidation by HO radical will be relatively rapid: half-lives of one to two months in the

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Table 15

PRODUCERS AND LOCATIONS FOR POLYHALOMETHANES

Product	Producer	Location
Carbon tetrachloride	Allied Chemical Corp.	Moundsville, West Virginia
	Dow Chemical Co.	Freeport, Texas Pittsburg, California Plaquemine, Louisiana
	E.I. du Pont de Nemours and Co., Inc.	Corpus Christi, Texas
	FMC Corp.	South Charleston, West Virginia
	Stauffer Chemical Co.	Le Moyne, Alabama Louisville, Kentucky Niagara,Falls, New York
	Vulcan Materials Co.	Geismar, Louisiana Wichita, Kansas
Chloroform	Allied Chemical Co.	Moundsville, West Virginia
	Diamond Shamrock Corp.	Belle, West Virginia
	Dow Chemical Co.	Freeport, Texas Plaquemine, Louisiana
	E.I. du Pont de Nemours and Co., Inc.	Niagara Falls, New York
	Stauffer Chemical Co.	Louisville, Kentucky
	Vulcan Materials Co.	Newark, New Jersey Wichita, Kansas

Table 16

PHYSICAL AND CHEMICAL PROPERTIES OF POLYHALOMETHANES

Compound/Synonyms	Mol. Wt.	M.P. (^{o}C)	B.P. (^{o}C)	Density	n_D	Vapor Pressure, mm(^{o}C)	Solubility
Carbon tetrachloride; tetrachloromethane	153.82	-22.96	76.75^{760}	1.5942^{20}_{4}	1.4664^{20} 100(23) 40(4.3)	400 (57.8)	Insoluble in water, soluble in alcohol, infinitely soluble in ether, benzene, and chloroform
Chloroform; trichloromethane	119.38	-63.5	61.2^{760}	1.4916^{18}_{4}	1.4433^{25}	400 (42.7); 100 (10.4)	Slightly soluble in water, soluble in acetone, infinitely soluble in alcohol, ether, and benzene

troposphere seem likely, giving $COCl_2$ or $COBr_2$. These products may be washed out in rain where they will hydrolyze to CO_2 and HCl or HBr.

Bioaccumulation

The saturated hydrocarbons, methyl chloride, chloroform, and carbon tetrachloride, have log P values of 1.92, 1.92, and 2.70 respectively. Carbon tetrachloride concentrates rapidly in adipose tissue (McCollister, et al., 1951; Reynolds, 1967; Rao and Rechnagel, 1969) and has a long biological half-life as indicated by detectable amounts found by Stewart and coworkers (1961) in the expired air of human patients two weeks after exposure to CCl_4 vapor.

Chloroform also concentrates rapidly in fat. Cohen and Hood (1969) administered ^{14}C-labeled chloroform by inhalation to mice for 10 minutes, and sacrificed the animals 0, 15, and 120 minutes after exposure by immersion in liquid nitrogen. They prepared autoradiograms of longitudinal sections of the body and also analyzed samples of selected tissues for radioactivity. The tissues analyzed were blood, brain, muscle, lung, kidney, liver, fat, and brown fat. In animals sacrificed immediately after exposure, the total concentration of radioactivity in these tissues was 6550 counts/min/mg, with 25.6% in fat and 48.2% in brown fat. In animals sacrificed 15 minutes after exposure, these tissues contained a total of 3270 counts/min/mg of which 29.1% resided in fat and 45.6% resided in brown fat. The tissues from animals killed 120 minutes after exposure contained 922 counts/min/mg or about 14% of that found in the animals killed immediately after exposure. In these animals, 78.8% of the radioactivity was distributed fairly evenly among the liver (27.1%), fat (28.8%), and brown fat (22.9%).

We found no information on methyl chloride; however, because its log P value is the same as that of chloroform, we believe that it may also accumulate in animal tissues.

10. AROMATIC AMINES

Production and Properties

Most of the compounds in this group have been the subject of a previous report (Radding et al., 1975) and are important as intermediates for the production of dyes, antioxidants, or in polymers. Production figures are given below (in pounds per year).

4,4'-Methylenebis(2-chloroaniline)	7.7 million	(1972)
1-Naphthylamine	7 million	(1974)
3,3'-Dichlorobenzidine	4.6 million	(1972)
Benzidine	1.5 million	(1972)
2-Biphenylamine	<1000	(1974)
4-Biphenylamine	<1000	(1974)
4,4'-Methylenebis(2-methylaniline)	<1000	(1974)
2-Naphthylamine	<1000	(1974)

Producers and locations are given in Table 17. Synonyms and physical and chemical properties are given in Table 18.

Environmental Transformations

Most simple aromatic amines such as benzidine and aniline have sufficiently low vapor pressures and high solubility to minimize their transport to the atmosphere from water or sorption to sediments or organisms. In water their rates of oxidation by RO radical (if present) would be fast: $t_{\frac{1}{2}} \sim 100$ hours. Benzidines absorb in the solar region strongly below 350 nm (Bilbo et al., 1953) but no photochemistry is reported. Biodegradation may be an important fate for many aromatic amines in aquatic systems; however, benzidine and its derivatives are bacteriostatic.

Table 17

PRODUCERS AND LOCATIONS FOR POLYHALOMETHANES

Compound	Producer	Location
4,4'-Methylenebis(2-chloroaniline)	Anderson Development Co E. I. du Pont de Nemours & Co., Inc.	Adrian, Michigan Deepwater Point, New Jersey
1-Naphthylamine	American Hoechst Corp.	Coventry, Rhode Island
3,3'-Dichlorobenzidine (as hydrochloride)	Lakeway Chemicals, Inc. The Upjohn Co.	Muskegon, Michigan North Haven, Connecticut
Benzidine (as sulfate)	City Chemical Corp.	Jersey City, New Jersey
2-Biphenylamine	MacKenzie Chemical Works, Inc. Aceto Chemical Co., Inc.	Central Islip, New York Carlstadt, New Jersey
4-Biphenylamine	N.A.	N.A.
4,4'-Methylenebis(2-methylamine)	N.A.	N.A.
2-Naphthylamine	Sigma Chemical Co.	St. Louis, Missouri

Table 18

PHYSICAL AND CHEMICAL PROPERTIES OF AROMATIC AMINES

Compound	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ_{max} (log ε)	Solubility
4,4'-Methylenebis(2-chloroaniline); 4,4'-Methylenebis(2-chlorobenzamine); Bis(3-chloro-4-aminophenyl)-methane	267	110					
1-Naphthylamine; 1-aminonaphthalene; 2-naphthylamine; 2-naphthylamine	143.19	50	300.8^{760} 160 12 sublimes	1.1229^{25}_{25}	1.6703^{54}	242(4.27) 320(3.71) in alcohol	Slightly soluble in water; very soluble in alcohol and ether
Benzidine; 4,4'-diaminobiphenyl; C.I. Azoic Diazo Component 112; (1,1'-biphenyl)-4,4'-diamine	184.24	122-128	400^{740}			287(4.4) in alcohol	Slightly soluble in hot water, very soluble in alcohol and ether
2-Biphenylamine; 2-phenylaniline; 2-biphenylamine	169.23	51-3	299^{760}			300(3.5) in alcohol	Insoluble in water; soluble in alcohol, ether, and benzene
3,3'-Dichlorobenzidine; (1,1'-biphenyl)-4,4'-diamine,3',3'-dichloro-; C.I. 23060	253.13	132-3					Almost insoluble in water, readily soluble in alcohol and benzene
4-Biphenylamine; 4-phenylaniline; Zenylamine; 4-biphenylylamine	169.23	53.4	302 191^{15}			278(4.24) in alcohol	Slightly soluble in water; soluble in alcohol, ether, and chloroform
4,4'-Methylenebis(2-methylaniline); 4,4'-methylene-di-o-toluidine; 4,4'-methylenebis(2-methylbenzenamine)							
2-Naphthylamine; 2-naphthylamine; C.I. 37270	143.19	113	306.1	1.0614^{98}_{4}		236(4.78) 280(3.82) 292(3.73) 340(3.28) in alcohol	Very soluble in hot water, soluble in cold water, alcohol, and ether

In the atmosphere, oxidation by HO· to phenols and amine oxides, hydroxylamines and ring open structures is probably rapid. Chlorine substitution should have little effect on rates of oxidation in the atmosphere but may retard oxidation in water by RO radical.

Reliable data on the oxidation, photochemical, and sorption properties of aromatic amines in water are lacking and are badly needed for reliable assessment.

Bioaccumulation

The partition coefficient (log P) for benzidine is reported as 1.81. We calculated the log P to be 1.4. Both reported and calculated values indicate that benzidine should not accumulate appreciably in the body. This hypothesis is supported by data obtained by Kellner and coworkers (1973), who found in rats, dogs, and monkeys, almost no radioactivity in the tissues 7 days after intravenous administration of ^{14}C-labeled benzidine. They reported that although the urine of these animals contained benzidine, most of the radioactivity was associated with metabolites. Bradshaw and Clayson (1955), Clayson (1959), and Fabre (1960) identified these metabolites as 4'-acetoamido-4-aminodiphenyl, 3-hydroxybenzidine, 4,4'-diamino-3-diphenylyl hydrogen sulfate, 4'-acetamido-4-amino-3-diphenylyl hydrogen sulfate, 4'-amino-4-diphenylyl sulfamic acid, and N-glucuronides. They also found several acid-stable unknowns.

We calculated the partition coefficient for 3,3'-dichlorobenzidine (DCB) as 2.8. No empirically determined values were found in the literature. Our calculated value suggests that the compound has a slight propensity to accumulate in body tissues.

Kellner and coworkers (1973) reported that DCB is excreted almost unchanged in the urine of rats, dogs, and monkeys and that it is excreted less rapidly than benzidine. Aksamitnaya (1959) found four metabolites in the urine of rats given DCB orally over a long period and in a single large dose; one of the metabolites was benzidine. The compound has been identified in the urine of workers in a pigment plant (Akiyama, 1970).

Our calculated partition coefficient for α-naphthylamine is 1.8. The value reported in the literature is 2.15. The partition coefficient for β-naphthylamine is probably in the same range. Neither compound should accumulate significantly in body tissues. Both compounds are metabolized by a mixed-function oxidase. Both have also been detected in the urine of workers in factories where these compounds are manufactured (Takemura et al., 1972).

No information was found concerning the accumulation of 4,4'-methylene-bis(2-chloraniline) in animal tissues. It and certain metabolites have been identified in the urine of workers in plants where the compound is manufactured (Linch et al., 1971). The compound has a calculated partition coefficient of 3.5, and therefore may accumulate significantly in animal tissues.

We found no information concerning the fate or distribution of 4,4'-methylenebis(2-methyl)benzenamine in animals. It has a relatively high potential for bioaccumulation as indicated by its calculated log P value of 3.92.

11. POLYCHLORINATED BIPHENYLS

Production and Properties

Many polychlorinated biphenyls have been produced commercially under the names of Aroclor, Chlorextal, Dykanol, Inerteen, Noflamol, Pyranol, and Therminol. Most, however, are being phased out and at the present time Monsanto may be the only producer at the Sanget, Illinois, plant. In 1974, total production was estimated as 40 million pounds per year.

The physical properties of chlorobiphenyls (tetrachloro- or higher) are given in Table 19.

Environmental Transformations

Biphenyl and its chlorinated derivatives (PCBs) are lipophilic, nonvolatile, unreactive compounds that tend to bioaccumulate. They present a well-established environmental problem, and little can be added to what has already been summarized in several reviews of their pathways (Durfee et al., 1976). They are ubiquitous in the environment and persist for long periods in water. Evaporation to the atmosphere is also thought to be important. Some of the chlorinated and polychlorinated biphenyls starting with 4,4-dichlorobiphenyl will absorb above 300 nm. Crosby and Moilanen (1973) report that suspensions of these compounds in water undergo dechlorination and photohydrolysis to give 4-chlorobiphenyl, 4-chloro-4'-hydroxybiphenyl, and trace amounts of 2-chlorobenzofurans. Ruzo et al. (1972) and Herring et al. (1972) found similar photoreduction in hexane solvent or in neat mixtures.

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Table 19

PHYSICAL PROPERTIES OF CHLOROBIPHENYLS

Compound	Melting Point (°C)	Boiling Point °C (mm Hg)
3,4,3',4'-Tetrachlorobiphenyl	172	230 (50)
3,4,2',5'-Tetrachlorobiphenyl	103	
2,6,2',6'-Tetrachlorobipnenyl	198	
2,5,3',5'-Tetrachlorobiphenyl	162	
2,4,2',4'-Tetrachlorobiphenyl	83	
2,5,2',5'-Tetrachlorobiphenyl	84-85	
2,4,5,3',4'-Pentachlorobiphenyl	179	195-220 (10)
3,4,5,3',4',5'-Hexachlorobiphenyl	198	
2,4,6,2',4',6'-Hexachlorobiphenyl	111.5-112	
2,3,4,5,2',4',5'-Heptachlorobiphenyl		240-280 (20
2,3,5,6,2',3',5',6',-Octachlorobiphenyl	161	
2,3,4,5,6,2',3',4',5',6',-Decachlorobiphenyl	310	

Quantitative data on the fate of chlorinated biphenyls in aquatic systems are not yet available, but we think it is likely that photolysis will lead mainly to reduction in aquatic systems.

PCBs may be absorbed on particulates and dispersed in the atmosphere. In this form they may be oxidized by HO radical with half-lives in excess of 8 hours. Products would be phenols and quinones. Direct photolysis to less chlorinated products might also occur and would give products less susceptible to photolysis (shorter wavelength absorbance) but more reactive to HO radical ($t_{\frac{1}{2}} < 8$ hours). Again, the quantitative aspects of these reactions have not been examined.

Bioaccumulation

It is well-known that polychlorinated biphenyls accumulated in animal tissues and that some accumulate to a greater degree than others. Much of the knowledge of the environmental and health effects of PCBs is reviewed in the Proceedings of the National Conference of Polychlorinated Biphenyls (Ayer, 1976). We reviewed that report as well as many others, but have cited only a few that we feel are significant.

It appears that the degree of PCB accumulation in animal tissues increases with the number of chlorines attached to the biphenyl molecule. A survey conducted by Kutz and Strassman (In Ayer, 1976) of PBCs in adipose tissue of people living in the United States, showed that the most frequently encountered forms of PCBs are the penta-, hexa, and heptachlorobiphenyls.

Matthews and Anderson (1975) found that chlorobiphenyl, dichlorobiphenyl, pentachlorobiphenyl, and hexachlorobiphenyl are rapidly removed from the blood of rats after a single intravenous injection and stored initially in the liver and muscles. From the liver and muscles, PCB is redistributed to the skin and adipose tissue, and the rate of deposition in these tissues increases with the degree of chlorination. The rate of removal of these PCBs from the skin and adipose tissue, excretion in the urine, and total excretion decreases as the degree of chlorination increases. During the 42-day observation period, more than 90% of administered dose of mono-, di-, and pentachlorobiphenyls was excreted; however, these investigators calculated that less than 20% of the administered dose of hexachlorobiphenyl would ever be excreted. Excretion was not appreciable until the parent compound had been metabolized to more polar compounds.

These two studies indicate that the polychlorinated biphenyls with at least five chlorine molecules have the greatest potential for accumulating in animal tissues and that susceptibility to metabolic degradation to more polar compounds has a considerable influence in the magnitude of bioaccumulation of a compound. We calculated log P values of 7.24, 8.05, and 8.86 for tetrachloro-, pentachloro, and hexachlorobiphenyl, respectively. Although these values indicate that these PCBs have a very strong affinity for lipids, pentachloro- and perhaps tetrachlorobiphenyl are metabolized and excreted.

12. AZO DYES

Production and Properties

Azo dyes form the largest class of dyes and have found wide application in almost all manufactured goods. Estimated production is given below (in pounds per year) for the four compounds in this study.

2-Methyl-4-[(2-methylphonyl)-azo]-benzenamide	450,000	(1973)
4-Aminoazobenzene	330,000	(1974)
4-Dimethylaminoazobenzene	10,000	(1971)
Azobenzene	< 1,000	(1974)

Solvent dyes are produced by several companies; however, it is difficult to determine exactly which of the solvent dyes are produced by each company and where. Manufacturing sites and manufacturers are given below for the general class of solvent dyes.

Company	Site
Allied Chemical Company	Buffalo, New York
American Color and Chemical Corp.	Lock Haven, Pennsylvania
American Cyanamid Co.	Bound Brook, New Jersey
	Damascus, Virginia
	Marietta, Ohio
Atlantic Chemical Industries, Inc.	Nutley, New Jersey
Ciba-Geigy Corp.	McIntosh, Alabama
Dye Specialties, Inc.	Jersey City, New Jersey
GAF Corp.	Rensselaer, New York
Kewanee Industries, Inc.	Louisville, Kentucky
Morton-Norwich Products, Inc.	Paterson, New Jersey
Nyanza, Inc.	Ashland, Massachusetts
Passaic Color & Chemical Co.	Paterson, New Jersey
Hilton-Davis Chemical Co.	Cincinnati, Ohio

Physical and chemical properties along with synonyms are given in Table 20.

Environmental Transformations

Simple azobenzene dyes including azobenzene are polar and nonvolatile compounds that probably exhibit little propensity to transfer to the atmosphere from water. However, their high lipophilicity may lead to significant absorption by sediments having significant organic content.

Those azo dyes with primary amino groups, such as 4-aminoazobenzene, should exhibit chemical properties in water similar to those of aromatic amines including rapid oxidation by RO· to hydroxylamines and nitrosamines (Sections 28 and 29). The azo groups are strong chromophores that efficiently absorb visible and near UV solar radiation and may lead to a variety of photochemical transformations. Meier (1971) has provided a detailed discussion of the photochemistry of azo dyes and notes (p. 462) that very little information is available other than that both oxidation and reduction of azo dyes occur slowly and that oxygen inhibits reduction.

We conclude that, in aquatic systems where natural organics may be present in low concentrations of 5-10 ppm along with oxygen, photoreduction to hydrazines and amines is possible but is likely to be very slow except in oxygen-poor water. Some experiments to measure these rates are obviously needed. Biogradation is a likely fate along with bioaccumulation.

Dispersions of any azo dye in the atmosphere are likely to be oxidized by HO radical at rates comparable to those found for other aromatics, i.e., half-lives of 8 hours or less.

Table 20

PHYSICAL AND CHEMICAL PROPERTIES OF AZO DYES

Compound, Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ_{max} (log ε)	Solubility
2-Methyl-4-[(2-methylphenyl)azo] benzenamide; C.I. Solvent yellow 3; 4-(o-tolylazo)-o-toluidine; o-aminoazotoluene	225.28	101-102				326(4.28) 490(3.40) in alcohol	Insoluble in water, soluble in alcohol, ether, and chloroform
4-Aminoazobenzene; C.I. Solvent Yellow 1; 4-(phenylazo)-benzenamine						251(4.0) 384(4.4) in alcohol	Slightly soluble in hot water; soluble in hot alcohol, benzene, cold chloroform, ether
4-Dimethylaminoazobenzene; C.I. Solvent Yellow 2; N,N-dimethyl-4-(phenylazo)-benzenamine; butter yellow	225.30	117	Decomp.				Insoluble in water; soluble in ether, chloroform, benzene, petroleum ether, mineral acids, oils
Azobenzene; benzeneazobenzene; diphenyldiazene	182.23	71	293	1.20		243(4.02) 281(3.72) 433(3.18) in alcohol	Slightly soluble in water; soluble in alcohol, ether, and benzene

Bioaccumulation

The log P values for azobenzene, 4-aminoazobenzene, 4-dimethylaminoazobenzene, and 2-methyl-4-[(2-methylphenyl)azo] benzenamide are 3.82, 3.50, 4.58, and 4.24, respectively. These values indicate that these compounds are highly lipophilic. We did not find any information concerning their distribution or retention in animal tissues. These are probably good examples of the fact that highly lipophilic compounds are frequently metabolized extensively. Robinson and coworkers (1964) postulated that 4-aminoazobenzene may become bound in tissues, perhaps by a reaction between the amino group and tissue constituents. The compound is metabolized to a number of different compounds (Matsumoto and Terayama, 1962; Ishidate and Hashimoto, 1962); however, it does not undergo methylation to form more potent carcinogins such as 4-methylaminoazobenzene or 4-dimethylaminoazobenzene (Matsumoto, 1965).

4-Dimethylaminoazobenzene binds to DNA and other proteins (Warwick, 1969; Roberts, 1969; Chauveau and Benoit, 1973). Its metabolism has been extensively studied, and many of its biotransformation products have been identified.

We found no information on the distribution or retention of 2-methyl-4-[(2-methylphenyl)azo] benzenamine in animals. Its high log P value (experimental) suggests that it has a high tendency to bioaccumulate.

13. CARBAMIC ACID ESTERS

Production and Properties

Carbamates (or urethanes) are used in plastics, pesticides, pharmaceuticals, surface-active agents, dye intermediates, and corrosion inhibitors. Ethyl carbamate, the only compound considered here, is used as an intermediate in organic synthesis, in pesticide formulations, and as a solvent. Annual estimated production was 100,000 pounds per year in 1972.

Synonyms for ethyl carbamate are: carbamic acid, ethyl ester, and urethane. Physical and chemical properties are given below.

Molecular weight	89.10
Melting point (°C)	48.5-50
Boiling point (°C)	185^{760}
Density	0.9862^{21}_{4}
n_D	1.4144^{52}
Solubility	Very soluble in water, alcohol, ether, benzene, chloroform

Environmental Transformation

Simple carbamate esters such as ethyl carbamate are polar, soluble in water, and nonvolatile. They will not transfer to the atmosphere or absorb in sediments to any significant extent. Hydrolysis of carbamates to alcohol, amine or ammonia, and CO_2 is generally extremely slow at 25°C and pH 7. Half-lives for hydrolysis in Table 3 indicates that, with the exception of aromatic esters having an ArOC(O)NHAr structure, they will not hydrolyse at 25°C and pH 7 for centuries. Oxidation is also negligbly slow. Photohydrolysis of aromatic carbabates is a possible, faster process. Biodegradation may be a facile process for many carbamates, preventing their accumulation, but we have not looked for data on this process.

We estimate that in the atmosphere ethyl carbamate will oxidize with HO radical with a half-life of 47 hours. Products would probably include ammonia, CO_2, and acetaldehyde. Aromatic carbamates might photolyse, but we have found no data.

Bioaccumulation

Ethyl ester of carbamic acid, commonly called urethane, has an experimentally determined log P value of -0.75; therefore, bioaccumulation of this compound is not expected. Studies have shown that the compound or its metabolites binds with DNA (Pound and Lawson, 1976; Prodi et al., 1073; Lawson, 1974; Lawson and Pound, 1972, 1973); however, this is not evidence of bioaccumulation.

The compound is metabolized by laboratory animals (Nery, 1968; Grogan et al., 1970). Repeated administration stimulates metabolism of the compound (Braeunlich, 1968).

14. HYDRAZINES

Production and Properties

Hydrazines are used over a broad spectrum of industries ranging from agricultural chemicals, medicinals, textile agents, and plastics, to propellant mixes. The production figures for the compounds listed in this class are given below (in pounds per year).

Hydrazine	3.1 million (1971)
1,1-Dimethylhydrazine	< 1.1 million (1973)
Hydrazine carboxamide	> 1000 (1974)
1,2-Dimethylhydrazine	< 1000 (1974)

Producers and locations are as follows:

Compound		
Hydrazine	Fairmont Chemical Co.,Inc.	Newark, New Jersey
	Hummel Chemical Co., Inc.	South Plainfield, New Jersey
	Olin Corp.	Lake Charles, Louisiana
	Uniroyal, Inc.	Geismar, Louisiana
1,1-Dimethylhydrazine	FMC Corp.	Baltimore, Maryland
	Olin Corp.	Lake Charles, Louisiana
Hydrazine Carboxamide	Fairmount Chemical Co.,Inc.	Newark, New Jersey
	Olin Corp.	Rochester, New York
1,2-Dimethylhydrazine	N.A.	N.A.

Synonyms and physical and chemical properties are given in Table 21.

Environmental Transformations

Data on likely environmental fates of hydrazines are sparse. However, from their properties and from work in this laboratory we can make some reasonable assumptions as to likely pathways.

Table 21

PHYSICAL AND CHEMICAL PROPERTIES OF HYDRAZINES

Compounds, Synonyms	Mol. wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ_{max} (log ε)	Solubility
Hydrazine	32.05	1.4	113.5	1.011^{15}	1.470^{22}		Very soluble in cold water, soluble in alcohol
1,1-Dimethylhydrazine, dimazine; N,N-dimethylhydrazine	60.11		63^{752}	0.7914^{22}	1.4075^{22}		Very soluble in water, alcohol, ether
Hydrazine carboxamide; aminourea; carbazamide; carbamic acid, hydrazide; semicarbazide	75.07	96				231(1.2) in alcohol	Insoluble in ether, benzene, chloroform; soluble in alcohol; very soluble in water
1,2-Dimethylhydrazine; N,N′-dimethylhydrazine; hydrazomethane	60.11		81^{753}	0.8274^{20}_{4}	1.4209^{20}	235(4.0) 280(3.1) in alcohol	Infinitely soluble in water, alcohol, and ether

All the simple hydrazine derivatives are polar, nonvolatile, and soluble in water. As a result none of these compounds will transfer to the atmosphere at significant rates; nor are they likely to absorb to sediments in significant amounts.

In water, oxidation by molecular oxygen to diimides and then to nitrogen, possibly catalyzed by metal ions

$$RNHNH_2 \xrightarrow{O_2} [RN = NH] \rightarrow RH + N_2 + H_2O$$

(Wagnerova et al., 1973) may be the most important fate (Ross et al., 1971).

Methylhydrazine reacts rapidly with oxygen in the gas phase at concentrations of < 0.01 M ($t_{\frac{1}{2}} < 1$ hour), dimethylhydrazine more slowly, from which we conclude that these compounds will not persist in water or in the atmosphere. Oxidation by HO radical in the gas phase is reported to be rapid with a half-life of less than 1 hour (Hack et al., 1974).

Bioaccumulation

The log P values for hydrazine, 1,1-dimethylhydrazine, 1,2-dimethylhydrazine, and hydrazine carboxamide are negative, indicating that none of these compounds should accumulate in animal tissues. However, high levels of hydrazine and 1,1-dimethylhydrazine appear to impair kidney function. This could prevent normal excretion of these compounds and their metabolites and increase the overall body burden, which in turn would increase the probability of binding of the compounds to proteins or deposition in adipose tissue.

Hydrazine has a calculated log P value of -3.08. A study by Smith and Clark (1972) showed that hydrazine is rapidly absorbed into the blood stream of dogs but that blood levels decline slowly after reaching a peak. After administration of high levels of hydrazine, blood levels peaked and remained elevated. This suggested an impairment of detoxication and/or renal function. Continued elevated hydrazine blood levels can contribute to bioaccumulation. Mass action could increase the probability of binding of hydrazine to cellular constituents as well as of deposition of hydrazine in adipose tissue.

We found no pertinent information concerning hydrazine carboxamide. Its calculated log P value of -2.53 indicates that it should not normally bioaccumulate.

15. ACYL HALIDES AND KETENE

Production and Properties

While the compounds listed here do have some end-use as is, most are used as intermediates in the preparation of pharmaceuticals, pesticides, textile finishing compounds, and so on. Production estimates are given below (in pounds per year).

Benzoyl chloride	15,000,000
Diethylcarbamoyl chloride	15,000
Dimethylcarbamoyl chloride	<1000 (1974)
Ketene	N.A.

Producers and locations are as follows:

Compound	Producer	Location
Benzoyl chloride	Velsicol Chemical Corp. Hooker Chemical Corp. Stauffer Chemical Co.	Chattanooga, Tennessee Niagara Falls, New York Edison, New York
Diethylcarbamoyl chloride	Aldrich Chemical Co. Ashland Chemical Co.	Milwaukee, Wisconsin Great Meadows, New Jersey
Dimethylcarbamoyl chloride	Ashland Chemical Co.	Great Meadows, New Jersey
Ketene (as dimer)	Eastman Chemical Products, Inc. FMC Corp.	Kingsport, Tennessee Meadville, Pennsylvania

Synonyms and physical and chemical properties are given in Table 22.

Table 22

PHYSICAL AND CHEMICAL PROPERTIES OF ACYLATING AGENTS

Compound, Synonyms	Mol. wt.	M.P. °C	B.P. °C	Density	n_D	λ_{max} (log ϵ)	Solubility
Benzoyl chloride; benzoic acid, chloride; benzenecarbonyl chloride	140.57	0	197.2^{760} 71^{9}	1.2120_{4}^{20}	1.5537^{20}		Decomposes in water and alcohol; soluble in benzene and carbon disulfide; infinitely soluble in ether
Diethylcarbamoyl chloride; diethylcarbamic chloride; diethylcarbamyl chloride	135.60	186					Decomposes in hot water or hot alcohol
Dimethylcarbamoyl chloride; dimethylcarbamyl chloride; dimethylcarbamic chloride							
Ketene; carbomethene; ethonone; methylene ketene	42.04	-151	-56_{760} -41			330(1.0) gas	Decomposes in water, alcohol, and ammonia; slightly soluble in ether and acetone

Environmental Transformation

In water, acyl chlorides hydrolyze rapidly with half-lives of only a few seconds for benzoyl chloride to an hour or so for ethyl chloroformates (Table 3); dimethylcarbamyl chloride has a half-life of less than 5 minutes. In all cases hydrolysis products include HCl but otherwise are probably not harmful or persistent. Because of these compounds' high reactivity toward water, other processes cannot compete under most conditions in aquatic systems. Ring substituents in benzoyl chloride such as nitro or methyl can increase the rate by factors of five to ten (Hudson and Wardill, 1950).

In the atmosphere we calculate that half-lives for hydrolysis in moist air (50% humidity) will be about 40 times longer than in pure water assuming no special solvent effects. Thus half-lives will be 10 minutes, 3 hours, and 40 hours for benzoyl, dimethylcarbamyl chlorides, and ethyl chloroformate, respectively. Oxidation by HO radical will be an important process only for the chloroformate.

Ketene is a powerful acylating agent that reacts rapidly with a variety of nucleophiles under laboratory conditions to give, with H_2O, acetic acid and, with alcohols, acetate esters. In the aquatic environment these reactions probably are slow, but we have found no recent data on which to base reliable estimates of persistence. Photolysis of ketene in the UV region up to 320 nm gives CO and methylene (CH_2); methylene reacts rapidly ($k > 10^8\ M^{-1}\ s^{-1}$) with a wide variety of organic compounds including oxygen. Available data (Calvert and Pitts, 1967) suggest that photolysis in the atmosphere will be rapid ($t_{1/2} < 10$ hours) and will compete with oxidation by HO radical. Products probably include CH_2O, CO_2, and CO.

Bioaccumulation

Our literature search did not produce any information concerning the fate or distribution of benzyl chloride, dimethylcarbamoyl chloride, diethylcarbamoyl chloride, or ketene in animals. The log P values for these compounds indicate that their tendency to bioaccumulate is insignificant.

The calculated log P values for dimethylcarbamoyl chloride, diethylcarbamoyl chloride, and benzoyl chloride are -1.20, -0.12, and 0.97, respectively.

We could not calculate a log P value for ketene because of insufficient information; however, ketene is a reactive polar compound that would probably have a log P value of less than 1 and therefore is not expected to accumulate appreciably in animal tissues.

16. PHOSPHORIC ACID ESTERS

Production and Properties

In general, phosphoric acid esters are intermediates in synthesis, in organophosphorus insecticides, and as alkylating agents. The estimated production rates for 1974 for the two esters discussed here are given below (in pounds per year).

Diethyl phosphate	7 million	(1974)
Dimethyl phosphate	< 1000	(1974)

Triethyl phosphate is produced by Eastman Chemical Products, Inc., in Kingsport, Tennessee. Synonyms and physical and chemical properties are given in Table 23.

Environmental Transformation

Simple trialkylphosphates are nonvolatile, very polar, and water soluble. Transfer to the atmosphere will be negligible. Kinetic data for hydrolysis of several alkyl and aryl phosphates are listed in Table 3. Half-lives are generally over 1 year for all but the nitrophenyl phosphates (methyl parathion and parathion), and unless biodegradation of these esters is facile they will persist. Adsorption of the esters to sediments is probably unimportant, as is oxidation in water. Photohydrolysis of suitably substituted arylphosphates is much faster than thermal hydrolysis and might become important in oligotrophic waters (Mabey et al., 1976).

Rates of oxidation of phosphate esters by HO radical are similar to those for sulfate esters and other organic esters: very slow unless activating groups such as phenyl or long alkyl chains are present; half-lives are over 100 hours. Direct photochemical processes in the atmosphere are probably not important even for aromatic esters.

Table 23

PHYSICAL AND CHEMICAL PROPERTIES OF PHOSPHORIC ACID ESTERS

Compound, Synonyms	Mol. wt.	M.P. °C	B.P. °C	Density	n_D	Solubility
Triethyl phosphate; phosphoric acid; triethyl ester	182.16	-56.4	$215\text{-}6^{760}$ 103^{25}	1.0695_4^{20}	1.4053^{20}	Soluble in water with slight decomposition; Soluble in ether and benzene; very soluble in alcohol
Trimethyl phosphate; phosphoric acid, trimethyl ester	140.08	-42(α) -62(β)	197.2^{760} 85^{24}	1.2144_4^{20}	1.3967^{20}	Slightly soluble in alcohol; soluble in ether, very soluble in water

Bioaccumulation

The log P values for triethyl and trimethyl phosphate indicate that neither should bioaccumulate significantly. Triethyl phosphate is somewhat lipophilic as indicated by its experimentally determined log P value of 1.11. Trimethyl phosphate is slightly lipophilic, having an empirical log P value of -0.52.

17. AZIRIDINES

Production and Properties

Ethylenimine (aziridine) was discussed in Task Order Report I (Radding et al., 1975) and only an update is included here in addition to other aziridines. Estimated production for 1974 is given below (in pounds per year).

Ethylenimine	<4.8 million
1-Aziridineethanol	10,000
Propylenimine	>1,000

Ethylenimine is produced by Dow Chemical Company in Freeport, Texas. Physical and chemical properties and synonyms are given in Table 24.

Environmental Transformation

Hydrolyses of aziridines to amino alcohols generally and of ethylenimine (EI) specifically to give 2-hydroxyethylamine are acid-catalyzed processes for which there are no direct measurements at pH 7 and 25°C. However, kinetic analysis of the pK_a data for EI reported by Buist and Lucas (1957) and the data of Early et al. (1958) on hydrolysis of EI in strong acid provide an estimate of the persistence of EI under environmental conditions.

Ethylenimine is weakly basic ($pK_a = 8$); thus at pH 8 half of EI is protonated and at pH 7, 90% is protonated. Early (1958) found the rate constant for hydrolysis k_w of protonated EI to be 5.2×10^{-7} sec^{-1} at 25°C. Thus the persistence of EI at pH 7 in water is ∿ 370 hours, very similar to the persistence of epoxides. At pH 6 (CO_2-buffered) the half-life will be only slightly shorter because 99% of EI will be protonated rather than 90%; however, at pH 8 where only 50% of EI is protonated, the half-life will be nearly doubled. Other aziridines

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TABLE 24

PHYSICAL AND CHEMICAL PROPERTIES OF AZIRIDINES

Compound, Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ max (log ε)	Solubility
Ethylenimine; Aziridine; dehydroazirine; azirane;	43.07		56^{756}	0.8321^{20}_{4}			soluble in alcohol; very soluble in ether, acetone, and benzene; infinitely soluble in water and other organic solvents
1-Aziridinethanol; 2-(Hydroxyethyl)ethylenimine; N-(2-hydroxyethyl)aziridine; 2-(1-aziridinyl)ethanol							
Propylenimine; 2-methylaziridine; 2-methylethylenimine			$66\text{-}67^{75}$	0.812^{16}			

should hydrolyze at nearly the same rate as EI based on the similarity of rates for most aliphatic epoxides (see above), but no specific rate data were found.

Oxidation of EI in water by RO· is probably very slow. Although EI is volatile, escape to the atmosphere probably will be very slow because of the basicity and polarity of EI. Similarly sorption to sediments or organisms will be low. Good data on physical transport processes for aziridines are lacking.

The fate of aziridines in the atmosphere is expected to be oxidation by HO radical with $t_{1/2}$ of 56 hours for aziridine and methylaziridine but 22 hours for aziridineethanol. No photochemical or hydrolytic processes appear important, but this conclusion could be modified if aziridines were absorbed on acidic particulates fly ash where hydrolysis would be a likely fate. No specific information is available on this matter.

Bioaccumulation

With the exception of ethylenimine, our literature search produced no information directly or indirectly concerned with bioaccumulation of the three aziridines. The log P values of these aziridines were less than zero, which indicates that they tend to be hydrophilic and therefore should have little tendency to bioaccumulate.

For ethylenimine, we calculated a log P value of -1.12. According to Wright and Rowe (1967), this compound is rapidly excreted by rats. About 55% of the injected dose was excreted in 96 hours. The kidneys play a major role in the excretion of this compound. Unexcreted ethylenimine was found evenly distributed throughout the body; very little was found in fatty tissue.

The calculated log P value for propylenimine is -0.46. We do not expect this compound to accumulate in fatty tissue.

1-Aziridineethanol is slightly more hydrophilic than ethylenimine and has a calculated log P of -1.79. It should not accumulate in fatty tissue.

18. LACTONES

Production and Properties

β-Propiolactone was discussed in Task One Report (Radding et al., 1975) and only an update is included here. Production has been estimated at less than 1000 pounds per year for 1974.

Synonyms for β-propiolactone are: 3-hydroxy propanoic acid and lactone. Physical and chemical properties are given below.

Molecular weight	72.06
Melting point (°C)	-33.4
Boiling point (°C)	162 decomposition, 51^{10}
Density	1.1460_{5}^{20}
n_D	1.4105^{20}
Solubility	Decomposes in water and alcohol; soluble in chloroform; infinitely soluble in ether

Environmental Transformation

Lactones are subject to rapid hydrolysis in aquatic systems. A careful study of the hydrolysis of β-propiolactone (PL) to give 3-hydroxypropionic acid was made by Long and Purchase (1950). The reaction is rapid at 25°C, independent of acidity, and only weakly catalyzed by hydroxide ion. Based on the rate constant for hydrolysis in neutral water (k_w) of 3.3 10^{-3} min^{-1}, we estimate the half-life of PL in water at 25°C and pH 7 to be 3.5 hours and appreciably less in ocean or brackish water where chloride ion will also cleave the lactone ring. Base-catalyzed hydrolysis is not important to PL until the pH reaches 11 (k_b = 100 liter mol^{-1} min^{-1}). Butyrolactone is reported by the same workers to be only a fourth as reactive as PL. We expect higher lactones to resemble butyrolactone in their reactivity toward water at pH 7.

Oxidation of lactones by RO· in water are estimated to have half-lives of over 20 years.

The high boiling points, high solubilities, and polarities, coupled with the rapid hydrolysis rates in water, make it likely that the major fate of lactones will be to remain in water to hydrolyze to the hydroxy acids.

If released in the atmosphere, lactones will be oxidized to mixtures of bifunctional 1-, 2-, and 3-carbon compounds with half-lives of ∿ 100 hours. Rain is likely to wash out lactones to soil and streams. Photochemical cleavage of lactones in the atmosphere seems unlikely since they have no significant absorption in the solar region.

We uncovered no information concerning bioaccumulation of β-propiolactone. However, it has a partition coefficient of -0.3 (calculated), is rapidly hydrolyzed, and is highly reactive. These factors strongly suggest that it does not accumulate in tissues.

19. ALKYL SULFATES

Production and Properties

Both the dimethyl and the diethyl sulfates are used as alkylating agents. Production estimates for 1974 show greater than 1000 pounds per year manufactured for both.

Dimethyl sulfate is produced by E.I. du Pont de Nemours & Co., Inc. at Bell, West Virginia, and at Linden, New Jersey. Diethyl sulfate is produced by Union Carbide Corporation at Texas City, Texas.

Synonyms and physical and chemical properties are given in Table 25.

Environmental Transformation

Sulfate esters are relatively polar and nonvolatile compounds that are not likely to transfer to the atmosphere from water. Hydrolysis of sulfates at pH 7 and 25°C is a facile process (see Table 3) with half-lives of only 1 to 2 hours for ethyl and methyl sulfates. Cyclic sulfates are also readily hydrolyzed under these conditions. Some data on sulfonate esters, included for comparison, show that they are much more resistant to hydrolysis ($t_{1/2}$ ∿17-40 hours). The product sulfuric or sulfonic acids would be damaging only in concentrated spills. Oxidation of these esters in water is negligible, as is bioaccumulation and absorption to sediments.

Simple alkyl sulfates in the atmosphere would wash out in rain and hydrolyze. Oxidation by HO radical would be very slow for dimethyl sulfate and only moderately rapid for diethyl sulfate. Products probably would be sulfonic acid, CH_2O, CO, and CO_2.

Table 25

PHYSICAL AND CHEMICAL PROPERTIES OF ALKYL SULFATES

Compound/Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ max (log)	Solubility
Diethyl sulfate; Sulfuric acid, diethyl ester; ethyl sulfate; DES	154.19	-24.5	208(sl. decomp. 96^{15}	1.1774^{20}_{4}	1.4004^{20}		Insoluble in cold water; decomposes in hot water and in hot alcohol; infinitely soluble in alcohol and ether
Dimethyl sulfate; sulfuric acid, dimethyl ester; methyl sulfate; DMS	126.13	-31.75	188.5^{760}	1.3283^{20}	1.3874^{20}	265 (undil.)	Insoluble in carbon disulfide; soluble in water, ether, and benzene; infinetely solution in alcohol

Bioaccumulation

Dimethyl sulfate and diethyl sulfate are strongly lipophobic and are not expected to bioaccumulate. Dimethyl sulfate is rapidly broken down in the body. Diethyl sulfate may behave similarly; however, we found no information concerning its fate in biological systems.

Our calculated log P value for dimethyl sulfate and diethyl sulfate are -4.26 and -3.18, respectively. Swann (1968) reported that the dimethyl sulfate disappears completely from the blood of rats within three minutes after intravenous injection. The concentration in the blood one minute after injection was one-sixth of that expected if the compound had distributed itself evenly in body water; hence, the author concluded that the compound undergoes rapid breakdown.

20. SULTONES

Production and Properties

Sultones are becoming increasingly important as intermediates in organic synthesis to introduce sulfo-groups into materials. Production of each in 1974 was estimated at less than 1000 pounds per year.

Synonyms for the propane sultone are: 1,2-oxathiolane, 2,2-dioxide and 3-hydroxy-1-propanesulfonic acid, gamma-sultone. For butane sultone, there is: 1,2-oxathiane, 2,2-dioxide; 4-hydroxy-1-butanesulfonic acid, delta sultone; and delta-valerosultone.

Environmental Transformations

These cyclic esters of hydroxysulfonic acids are very polar and nonvolatile. Like lactones, these esters hydrolyze relatively quickly in neutral water by a base-catalyzed process, the rate of which depends on ring size: 1,3-sultones hydrolyze about 40 times as fast as 1,4-sultones compared with a factor of only 4 times for lactones. Bordwell et al., (1959) showed that methyl substituents on 1,3-sultones retarded the rate of hydrolysis for steric reasons, and we can probably generalize that observation to include other substituents particularly in the α and β (to oxygen) positions. The rate effect of methyl groups is substantial: about 200 times for α,β trimethylsulfone.

The atmospheric chemistry of sultones is unknown; hydrolysis in moist air is negligibly slow. We have estimated that oxidations by HO radical will be slow with half-lives over 50 hours.

Bioaccumulation

We did not find any information on the uptake, fate, distribution, excretion, or accumulation of 1,3-propane sultone or 1,4-butane sultone in biological systems. 1,3-Propane sultone is hydrophilic and

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not expected to accumulate in body tissues. For this compound, we calculated a log P value of -2.82. Like 1,3-propane sultone, 1,4-butane sultone is hydrophilic and has a calculated log P of -2.45.

21. ARYL DIALKYLTRIAZENES

Production and Properties

Triazenes are used not only as intermediates, but also as herbicides, rodent repellents, and as antineoplastic agents. Production for 1974 has been estimated at less than 1000 pounds per year for both 1-phenyl-3,3-dimethyltriazene and 1-(4-chlorophenyl)-3,3-dimethyltriazene considered here.

Synonyms are given below for each compound.

- 3,3-Dimethyl-1-phenyltriazene;
  1-phenyl-3,3-dimethyltriazene
- 1-(4-Chlorophenyl)-3,3-dimethyltriazene;
  1-(4-Chlorophenyl)-3,3-dimethyl-1-triazene

Environmental Transformation

The most reliable data relating to environmental chemistry of triazenes are those of Kolar and Preussmann (1971) on the hydrolysis of 14 substituted 1-aryl-3,3-dimethyltriazenes at 37°C and pH 7. They reported half-lives ranging from 10 minutes for p-MeO-phenyl to 250 days for m-NO_2-phenyl ; the phenyl dimethyltriazene has a half-life of 210 minutes, and p-chlorophenyl dimethyltriazene has a half-life of 40 to 45 hours. No temperature dependence is given, but we estimate that half-lives would increase by about a factor of 2 at 25°C.

Triazenes absorb strongly ($\varepsilon > 10{,}000$) around 310-360 nm and exhibit fairly rapid phototransformations in organic solvents (Le Fèvre and Liddicoet, 1951). These workers described photolysis of many aryl dimethyltriazenes on exposure to 4 hours of sunlight. From their data, we estimate that half-lives of several triazenes including phenyl dimethyltriazene may be as short as 100 hours. Products are not known; nor do we know the effect of solvent on the rate of the photoprocess. In the unlikely event that a triazene were dispersed into the atmosphere, it would be rapidly oxidized by HO radical ($t_{\frac{1}{2}} < 4$ hours). Products in part would consist of phenols, but some attack at the triazene structure is likely.

Bioaccumulation

We found no information directly or indirectly concerned with bioaccumulation of 3,3-dimethyl-1-phenyltriazene or 1-(p-chlorophenyl)-3,3-dimethyltriazene. Experimentally determined log P values for these compounds indicate that they may accumulate in fatty tissue. 3,3-Dimethyl-1-phenyltriazene has a log P value of 2.59, and the experimentally determined log P value for the o-chloro isomer of 1-(p-chlorophenyl)-3,3-dimethyltriazene is 3.00.

22. DIAZOALKANES

Production and Properties

Diazoalkanes are powerful alkylating agents. Only diazomethane was selected to represent this class of compounds. Production of diazomethane was estimated at less than 1000 pounds per year in 1974. Synonyms, physical and chemical properties are given below.

Compound, Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	λ max (log ε)	Solubility
Diazomethane;	42.04	-145	-2.3	380(0.5)	Decomposes in water; soluble in hot alcohol; soluble in ether
Azimethylene				408(0.5) 435(0.5) Gas	

Environmental Transformations

The simplist diazoalkane, diazomethane, is a yellow explosive gas, only slightly soluble in water. The extreme reactivity of diazomethane toward acids, metal ions, surfaces, and visible light makes it unlikely that diazomethane or other simple diazoalkanes will ever constitute a significant environmental pollution problem. In water we would expect rapid decomposition on reaction with natural organics and with particulates to remove it quickly, but we know of no quantitative data. Higher diazoalkanes particularly phenyl and diphenyldiazomethane are much less reactive in general, but also exhibit strong visible absorbance and might persist except for photolysis.

In the atmosphere diazomethane will photolyze fairly rapidly owing to a very broad absorbance band from 320 to 540 nm ($\epsilon \sim M^{-1}\ cm^{-1}$) (Brinton and Volman, 1951; Pitts and Calvert, 1967). Decomposition of diazomethane on particulates is also a reasonable possibility.

Bioaccumulation

We did not find any information on the fate of diazomethane in biological systems; nor were we able to calculate a log P value for it because of insufficient data. The compound is reactive and polar and probably would have a log P of less than 1. We do not expect it to accumulate significantly.

23. HALOALCOHOLS

Production and Properties

Haloalcohols are used as solvents and as intermediates, for example, in the preparation of insecticides. Production has been estimated as less than 1000 pounds per year in 1974 for 2-chloroethanol, which is produced by Union Carbide Corporation at Institute and South Charleston, West Virginia. 1-Chloro-2-propanol is produced by Eastman Kodak Company at Rochester, New York, and by R.S.A. Corporation at Ardsley, New York.

Synonyms and physical and chemical properties are given in Table 26.

Environmental Transport

Haloalcohols are discussed in Section 7 as alkyl halides.

Bioaccumulation

We found no information on the distribution or retention of 2-chloroethanol or 1-chloro-2-propanol in animal tissues. The experimentally determined log P value for 2-chloroethanol is 0.03, and the calculated log P value for 1-chloro-2-propanol is 0.06. These values indicate that neither compound should accumulate significantly in animal tissues.

Table 26

PHYSICAL AND CHEMICAL PROPERTIES OF HALOALCOHOLS

Compound, Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ max (log E)	Vapor Pressure mm(°C)	Solubility
2-chloroethanol; 2-chloroethyl alcohol; ethylene chlorohydrin	80.52	-67.5	128^{760} 44^{20}	1.20027^{20}	1.44189^{20}		$10^{(303)}$ 1(-4)	Slightly soluble in ether; infinitely soluble in water, alcohol
1-Chloro-2-propanol; 10chloroisopropyl alcohol; propylene chlorohydrin	94.54	$126\text{-}7^{750}$		1.115^{20}_{20}	1.4392^{20}			Infinitely soluble in water, alcohol, and ether

24. HALOETHERS

Production and Properties

One of the compounds included in this class, bis(chloromethyl) ether was included in the Task One Report (Radding et al., 1975) and only an update is given here. Haloethers have been used as textile finishing agents, as chloromethylation agents in organic synthesis, and even as solvents. Estimations of production for 1974 are given below (in pounds per year).

Chloromethyl ether	> 1000
Bis(chloromethyl)ether	< 1000
Bis(2-chloroethyl)ether	< 1000

Producers and locations are given below.

Compound	Producers	Location
Chloromethylmethyl ether	Stauffer Chemical Co.	Edison, New Jersey
Bis(2-chloroethyl)ether	Buckman Laboratories	Cadet, Missouri Memphis, Tennessee

Synonyms and physical and chemical properties are given in Table 27.

[illegible]onmental Transformation

The carcinogenic properties of bis(chloromethyl)ether (BCME) have prompted some studies of its chemical properties in the past two years with the result that reliable estimates can be made of its rates of hydrolysis and formation under environmental conditions. A few data on the monochloroether are also available.

Hydrolysis of BCME is complicated by its reformation from H_2O, CH_2O, and HCl through a series of rapid reversible reactions. The data of Frankel et al. (1974) indicate that the net equilibrium constant is nearly 10^{-7}. Thus

$$K = BCME/(CH_2O)(HCl) = 10^{-7}$$

with 4000 ppm CH_2O and 40,000 ppm HCl, about 13 ppm of BCME were found at equilibrium.

Hydrolysis of BCME in water is driven by the large excess of water (55 M) with the result that, by careful measurements on 1 ppm BCME dissolved in water, Tou et al., (1974) showed that hydrolysis of BCME is pH independent and that the rate constant at 20°C is 0.018 sec^{-1}. Thus, the half-life of BCME at 20°C in water is only ∿ 38 seconds. In moist air (50% relative humidity) Tou and Kallos (1974) found that k_1 = 00047 min^{-1}, corresponding to $t_{1/2}$ = 25 minutes.

IF BCME were spilled in any quantity into water, its low solubility (ppm range) would minimize hydrolysis except at the interface and promote volatilization. In the atmosphere, oxidation by HO· to products such as formic acid, CO, and CO_2 is likely to be slow ($t_{1/2} = \geq$ 100 hours) but may compete with hydrolysis at low humidity levels. No direct photolytic processes can be important; however, formaldehyde formed on hydrolysis porbably photolyses rapidly ($t_{1/2}$ < 2 hours), thus preventing reformation of BCME.

Solvolysis of methyl chloromethyl ether to HCl, CH_2O, and CH_3OH is extremely rapid. Jones and Thornton (1967) reported that at 25°C in 10 percent dioxane the half-life is only 2.3 seconds. Nichols and Merritt (1973) claim the relative reactivities of mono- and bis(chloromethyl) ether are over 5000/1 in dioxane-water. In pure water the half-life is probably <0.1 second, and in moist air the half-life would be <4 seconds. On this basis the persistence of the chloroether in water or air is fleeting and should not constitute an environmental pollutant except under very arid conditions.

Table 27

PHYSICAL AND CHEMICAL PROPERTIES OF HALOETHERS

Compound/Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λ max (log E)	Solubility
Chloromethylmethyl ether; chloromethoxymethane; methoxymethyl chloride	80.52	-103.5	59.15^{760}	1.0605^{20}	1.3974^{20}		Decomposes in water; soluble in alcohol, ether, acetone, and chloroform
Bis(2-chloroethyl)ether; 2,2'-dichloroethyl ether; 1,1'-oxybis(2-chloroethane); 1,1'-dichloroether	143.02	-24.5	178^{760} 75^{20}	1.2199^{20}_{4}	1.4575^{20}		Insoluble in water, slightly soluble in hot water; soluble in alcohol, ether, and acetone; infinitely soluble in benzene and methanol
Bis(2-chloromethyl) ether; oxybis(chloromethane); chloromethyl ether	114.96	-41.5	104^{760}	1.328^{15}_{4}	1.435^{21}		Decomposes in water; infinitely soluble in alcohol and ether

Bioaccumulation

Based on the calculated octanol/water partition coefficients (log P), bis(chloromethyl)ether, bis(2-chloroethyl)ether, and chloromethylmethyl ether show little or no propensity towards accumulating in body tissues. Bis(chloromethyl)ether has a calculated log P value of -.0.38; chloromethylmethylether, -0.21; and bis(2-chloroethyl)ether, 0.70. This last value indicates that bis(2-chloroethyl)ether is slightly lipophilic, but not enough to cause bioaccumulation problems. Our search did not produce any experimental data concerning the distribution of these compounds in tissues or organs.

25. HYDROXYLAMINES

Production and Properties

Hydroxylamines are widely used in the preparation of other intermediates in the chemical industry. The estimation of production for the year 1974 for each of the three compounds considered in this class is less than 1000 pounds per year.

Producers and locations are given below for hydroxylamine as both the hydrochloride and sulfate salts as well as for N-methylhydroxylamine and O-methylhydroxylamine.

Compound	Producer	Location
Hydroxylamine	G. Frederick Smith Chemical Co.	Columbus, Ohio
	Dow Badische Co.	Freeport, Texas
	Commercial Solvents Corp.	Sterlington, Louisiana
	Virginia Chemical Inc.	Portsmouth, Virginia
N-Methylhydroxylamine	Aldrich Chemical CO.	Milwaukee, Wisconsin
O-Methylhydroxylamine	Eastman Kodak Co.	Rochester, New York

Synonyms and physical and chemical properties are given in Table 28.

Environmental Transformations

Because they are polar and water soluble, hydroxylamines should not transfer from water to the atmosphere or to sediments at significant rates. Oxidation in water by RO radicals may be rapid, but there are no reliable data.

TABLE 28

PHYSICAL AND CHEMICAL PROPERTIES OF HYDROXYLAMINES

Compound, Synonyms	Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	n_D	λmax (log ε)	Vapor Pressure mm(°C)	Solubility
Hydroxylamine	33.03	33.05	56.5	1.204			10(47.2) 1 (solid)	Decomposes in hot water; soluble in cold water, acids, alcohol; very slightly soluble in ether, chloroform, benzene, and carbon disulfide
N-Methylhydroxylamine; N-Hydroxymethanamine;	47.06	42	62.5^{15}	1.0003_{4}^{20}	1.4164^{20}			Slightly soluble in ether and benzene; very soluble in water, methanol, and ethanol
O-Methylhydroxylamine; methoxyamine	47.06		49.50					Miscible with water, alcohol, and ether

Oxidation in air by HO radical should be rapid; the aminoxy radicals can further react to give NO and/or NO_2, but we know of no experimental data for these processes.

Bioaccumulation

We did not find any information concerning the distribution of hydroxylamine or of N-methyl- or O-methylhydroxylamine in organs and tissues. Our calculated log P values for these compounds indicate that they should not bioaccumulate. The calculated log P values for hydroxylamine, N-methylhydroxylamine, and O-methylhydroxylamine are -3.18, -2.90, and -2.47, respectively. The metabolism of these compounds, particularly hydroxylamine, has been studied (Kadlubar et al.,1973; Neunhoeffer, 1973).

26. NITROSAMINES

Production and Properties

Nitrosamine derivatives are used, for example, as fuel additives, antioxidants, pesticides, plasticizers, and in rocket fuels. The two nitrosamines considered here are estimated to be produced at <1000 pounds per year. Synonyms and physical and chemical properties are given in Table 29.

Environmental Transformation

Simple nitrosamines, particularly dimethylnitrosamine (DMNA), are volatile compounds readily formed from the parent amine and nitrous acid and are potent carcinogens (Lijinsky and Epstein, 1970). The high volatility of simple nitrosamines suggests that they will volatilize rapidly from water if formed there, but Tate et al. (1975) found that dimethyl, diethyl, and dipropyl nitrosamines appeared to be stable in soil and water at 250 or 20 ppm for up to 100 days in the dark. Some rapid initial loss of nitrosamines at 250 ppm due to volatilization to the atmosphere was noted, but biodegradation appears to be unimportant.

Hanst et al. (1976) calculated that in air DMNA would be formed rapidly from the amine and HNO_2: at 0.04 ppm of HNO_2, any added amine would form the DMNA at the rate of 2% hr^{-1}. However, photolysis of DMNA is rapid in sunlight with a half-life of less than an hour during most parts of the day to give CO, HO, CH_2O, and an unknown product. Photolysis of HNO_2 is also rapid. Most nitrosamines absorb strongly out to 360 nm and would be expected to photolyse rapidly also.

We calculate that direct oxidation of DMNA and higher nitrosamines by HO radical in the atmosphere would be relatively slow, and the evidence indicates that the dominant process for removal of nitrosamines from the atmosphere will be rapid photolysis. Recent ambient air analyses by Fine et al. (1976) confirm that little nitrosamine is present.

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Table 29

PHYSICAL AND CHEMICAL PROPERTIES OF NITROSAMINES

Compound, Synonyms	Mol. Wt.	B.P. °C	Density	n_D	λ max (log ε)	Solubility
Dimethylnitrosamine; N-nitrosadimethylamine; N-methyl-N-nitrosomethanamine; DMN, DMNA	74.08	154^{760}	1.0059_4^{20}	1.4358^{20}	231(3.85) 346(2.0) in alcohol	Soluble in water, alcohol, and ether
Diethylnitrosamine; N-ethyl-N-nitrosoethanamine;nitrosoethylamine; DENA; N-nitrosodiethylamine	102.14	176.9^{760}	0.9472_4^{20}	1.4386^{20}	233(3.7) 350(1.95) in alcohol	Soluble in water, alcohol, and ether

Photolysis of nitrosamines in water and other solvents has been investigated, but the results are in conflict. Chow (1964) and Burgess and Lavanish (1964) indicate that simple dialkylnitrosamines are nearly inert to photolysis in solvents. However, Sander et al. (1974) and Ballweg and Schmael (1967) report that several simple nitrosamines in water at low concentrations, including DMNA, photolyze rapidly in sunlight with half-lives of only a few hours.

Hydrolysis of nitrosamines occurs only in relatively acidic solvents and oxidation by RO· will be very slow.

Bioaccumulation

N-Nitrosodimethylamine and N-nitrosodiethylamine are potent carcinogens that are rapidly metabolized and have low log P values, indicating that the bioaccumulation potential of these compounds is low. The calculated log P value for N-nitrosodimethylamine is 0.06, which indicates that it shows nearly equal affinity for octanol and for water and should therefore not accumulate in body tissues.

There is evidence that both compounds can be synthesized in the body by bacterial flora. Grilli and coworkers (1975) observed binding of nitrosodimethylamine to DNA of the calf; and Swann and Magee (1968) reported evidence for alkylation of nucleic acids of the rat by the compound. There is evidence that the compound is synthesized in the intact animal from secondary amines and nitrite (Sen et al., 1969) and by bacteria in human saliva (Ishiwata et al., 1976).

27. NITROFURANS

Production and Properties

Nitrofuran derivatives are used as food additives, feed additives, and drugs. In 1974, the estimated production for the three compounds investigated was less than 1000 pounds per year for each. Synonyms and some physical and chemical properties are given below:

Compound/Synonyms	Mol Wt.	M.P. (°C)	B.P. (°C)	λ max (log)	Solubility
2-Nitrofuran	113.07	29	133.5^{123}	22.5(3.53) 3.5(3.91)	Soluble in water, alcohol, and ether

Environmental Transformation

Very little data were found to indicate the probable environmental pathways for these nitrofuran derivatives. As amides they will be stable for many years toward hydrolysis. 2-Nitrofuran undergoes photosubstitution by water to give the hydroxy compound (Groens and Havinga, 1974). Other thiazole nitrofurans should also be susceptible to this same transformation. The relatively intense absorption by nitrofuran around 310-320 nm ($\varepsilon > 10000$) (Raffauf, 1950) suggests that this process could be rapid for all nitrofurans. Unfortunately, no quantum yield data are available with which to calculate the actual rates of photolysis. If found in

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the atmosphere, they would probably oxidize with HO radical at rates comparable to those for other aromatic structures ($t_{1/2} < 8$ hours).

Bioaccumulation

We found no information concerning the distribution or retention of the three nitrofurans in animal tissues. 2-Nitrofuran, N-[4-(5-nitro-2-furanyl)-2-thiazolyl]-acetamide and formamide are metabolized by laboratory mammals, and reduced acetamide appears to bind to the sulfhydryl group of microsomal protein.

2-Nitrofuran shows a tendency to accumulate in animal lipids. This is suggested by its calculated log P value of 1.86. Paul et al. (1949) reported finding some unidentified metabolic products of 2-nitrofuran in the urine of rats to which the compound was administered orally; however, this study was not extensive enough to permit inferences regarding tissue accumulation.

N-[4(5-nitro-2-furanyl)-2-thiazolyl]-acetamide has a calculated log P value of -0.60, which suggests that the compound should not bioaccumulate. One of its metabolites appear to bind to microsomal protein sulfhydryl groups (Wang et al., 1975). The metabolite is not a deacylation product (Wang et al., 1974).

N-4-[(5-nitro-2-furanyl)-2-thiazolyl]-formamide is not lipophilic as indicated by its calculated log P value of -1.14. It should therefore not bioaccumulate. Wang and coworkers (1974) observed that the compound is deformylated in the stomach and intestines of a number of laboratory mammals.

28. AZIDES

Production and Properties

The only compound considered here is sodium azide, which is used as an intermediate. Estimate of production for 1974 was less than 1000 pounds per year. Physical and chemical properties are given below.

Mol. Wt.	M.P. (°C)	B.P. (°C)	Density	Solubility
65.01	decomp	decomp in vacuo	1.846^{20}	41.7 g/100 cc at 17°C in water 0.314 g/100 cc at 16°C in alcohol

Environmental Transformation

Inorganic azides are ionic solids with low vapor pressure and (in some cases) modest solubility in water. Alkali metal azides are relatively stable, but other metal azides are notoriously sensitive to detonation and are used as primary explosives in detonator caps. Simple azides such as sodium azide are stable in water in the dark but appear to be susceptible to photodecomposition with solar radiation. Data on solution photolysis are not susceptible to detailed analyses in terms of persistence in sunlight.

The chemistry of azides is ably summarized by Hudson et al. (1969). Photolysis of the solid azides produces metal nitrides initially and eventually the free metal and nitrogen (Verneker, 1967). We have found no information concerning the quantum yields for such processes or the effect of solution on the efficiency of the process. Burak et al. (1970) reported on the chemistry of photolysis of azide ion in solution using light of 214 nm; the chemistry is probably similar at higher wavelengths. No information is available to evaluate the reactivity of azides toward RO radical.

The likelihood that azide salts would be found in the atmosphere appears low except as particulate readily washed down with rain. Photolysis is a plausible pathway for removal of azides under those conditions, but we know of no data bearing on the matter.

Bioaccumulation

Sodium azide is a reactive, polar compound that should not accumulate significantly in animal tissues. We were not able to calculate its log P value because of insufficient data, but believe that the value should be less than 1. We found no data concerning the distribution or retention of this compound in animal tissues.

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